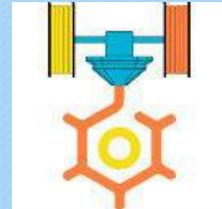




РОССИЙСКАЯ АКАДЕМИЯ НАУК
ЦЕНТР ФОТОХИМИИ

International Conference
“Organic & Hybrid Functional
Materials and Additive
Technologies”
(ChemTrends-2018)



Photoactive supramolecular devices and machines based on macrocyclic and unsaturated compounds

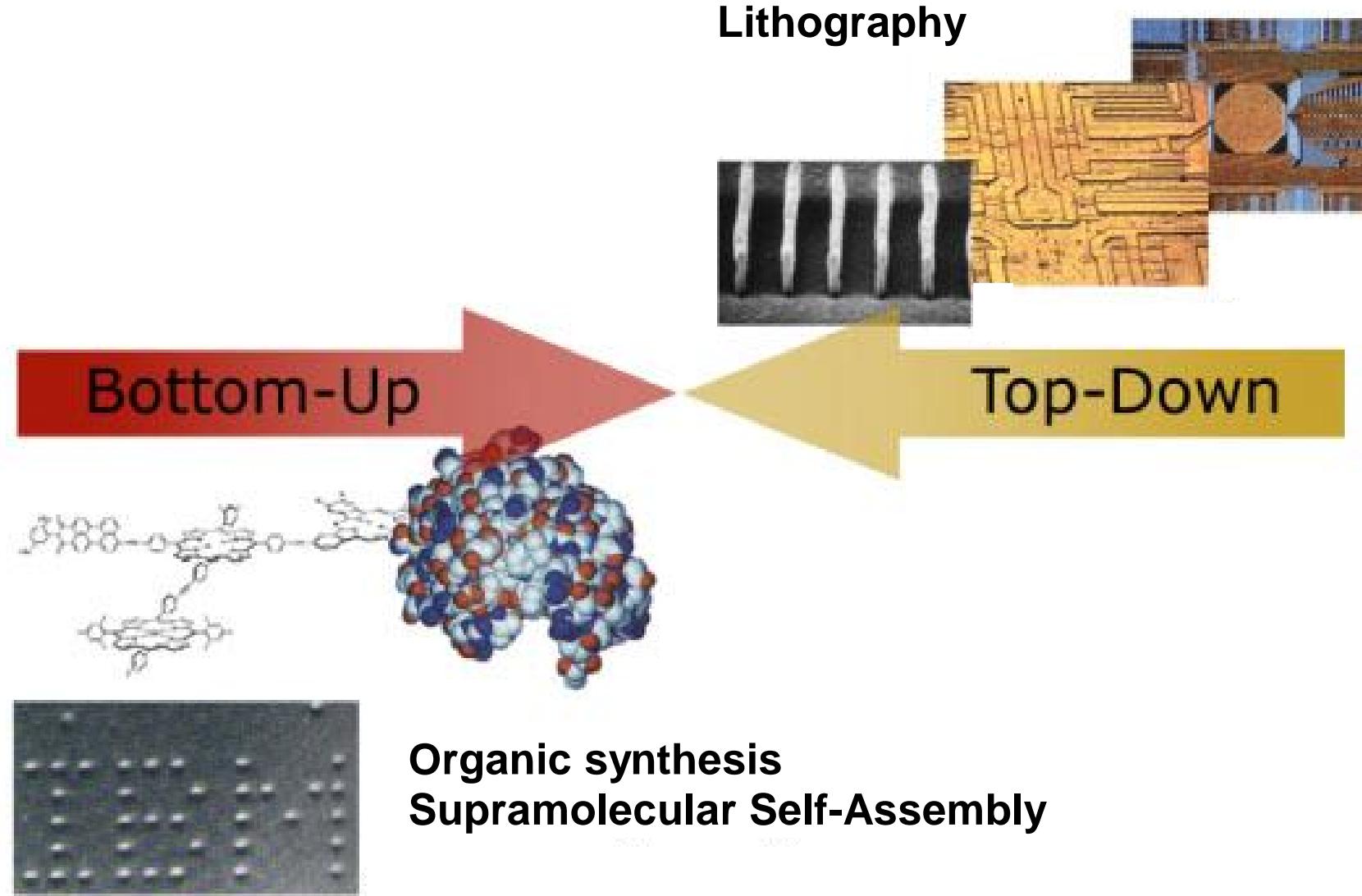
Prof. Sergey P. Gromov

<http://suprachem.photonics.ru>

<http://www.chem.msu.ru/rus/lab/organic/supra-nano.html>

NANOTECHNOLOGY “BOTTOM-UP”

STRATEGIES OF CREATION OF NANOSIZED ARCHITECTURES



SUPRAMOLECULAR DEVICES AND MACHINES

Supramolecular devices are structurally organized and functionally integrated chemical systems.

Systems that function as a result of mechanical motion of components relative to each other are called supramolecular machines.

J.-M. Lehn

They can be used:

“to design machines for energy and motion generation, conversion, and transmission at nanolevels, to devise a nanotool for the monitoring and diagnostics of nanoquantities of materials and substances.

Critical technologies of the RF

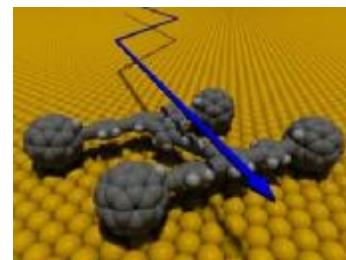
Means for control of supramolecular devices and machines

§ **Photoswitching** - $h\nu$

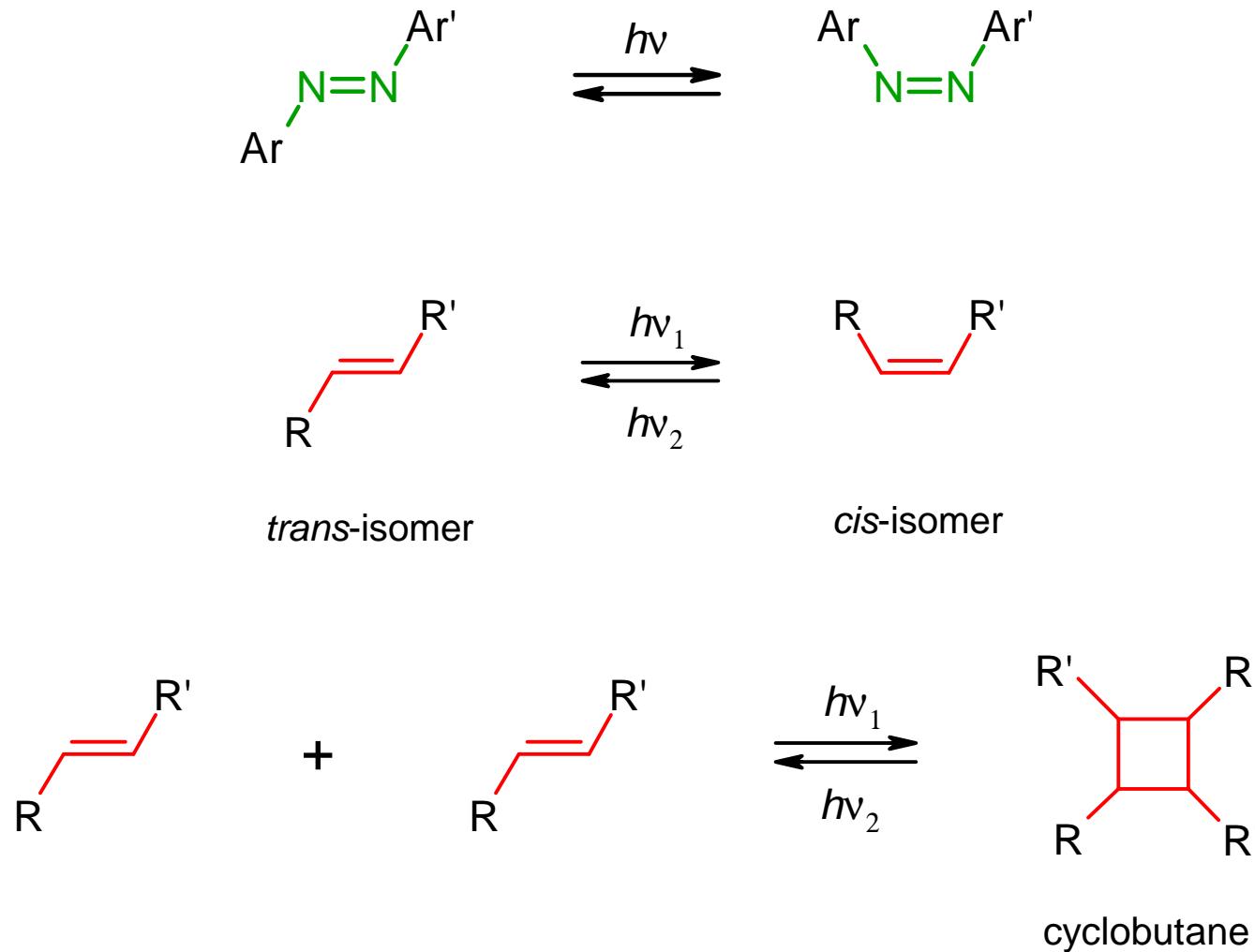
§ **Electrochemical switching** - e^-

§ **Chemical switching** - H^+, M^{n+}

§ **Thermal switching** - D



PHOTOANTENNAS OF SUPRAMOLECULAR DEVICES AND MACHINES BASED ON UNSATURATED COMPOUNDS

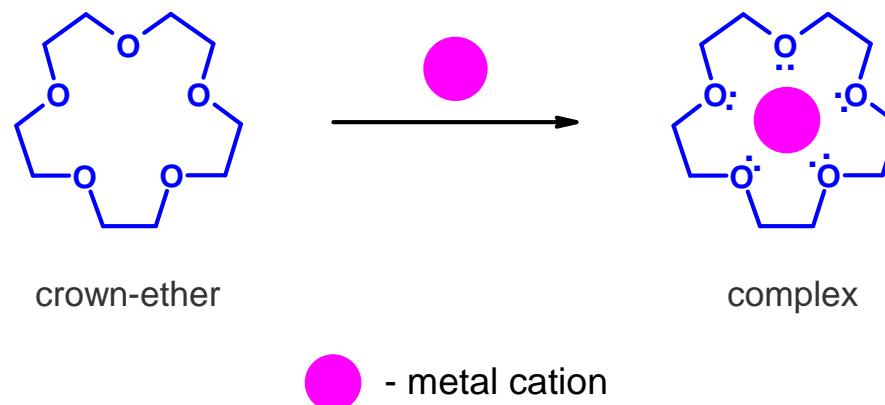


Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

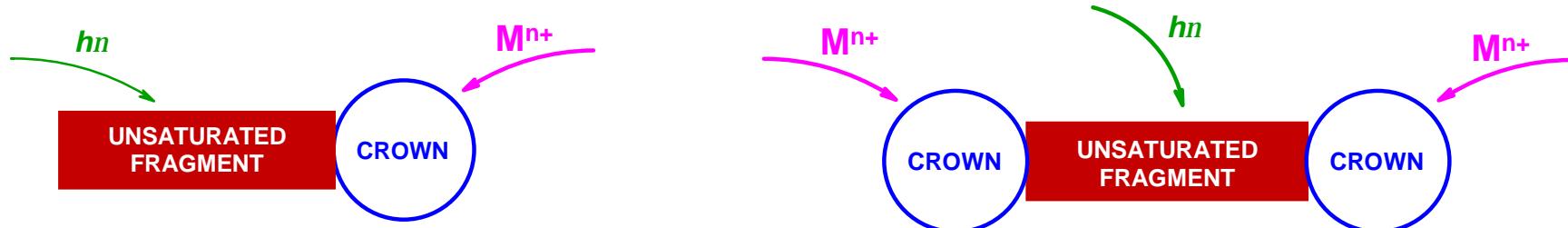
Gromov S. P. *Rev. J. Chem.* **2011**, 1, 1 (review);

Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, 84, 787 (review).

PHOTOSWITCHABLE SUPRAMOLECULAR DEVICES BASED ON UNSATURATED AND CROWN COMPOUNDS



● - metal cation

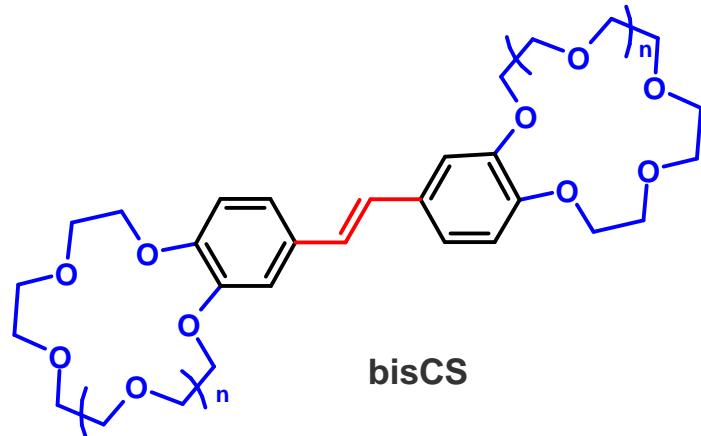
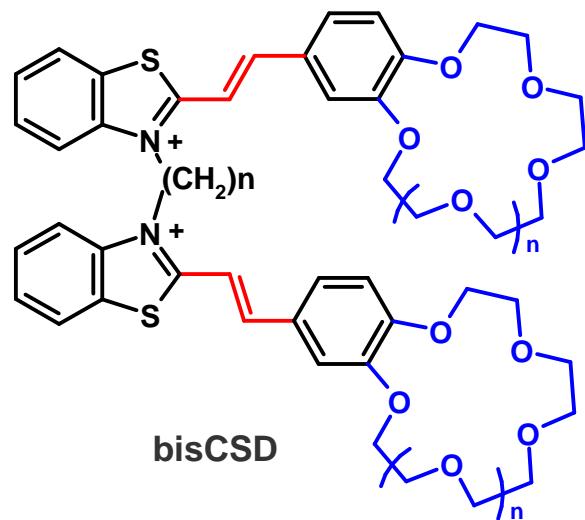
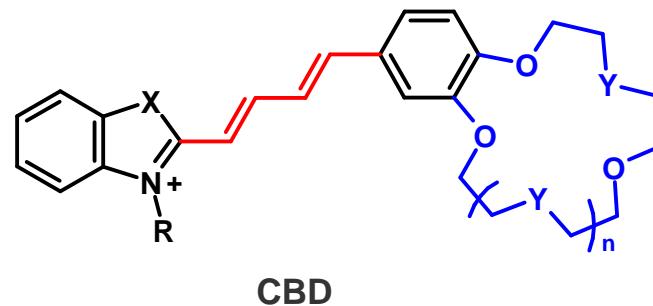
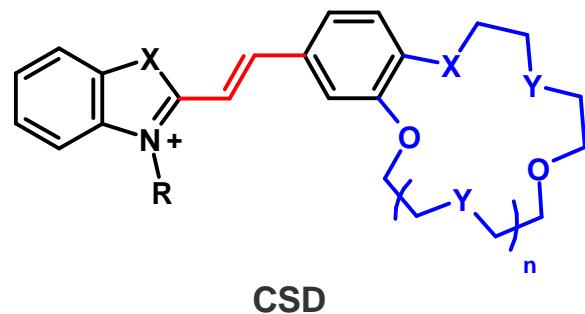


Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

Ushakov E. N., Alfimov M. V., Gromov S. P. *Russ. Chem. Rev.* **2008**, 77, 39 (review);

Alfimov M. V., Fedorova O. A., Gromov S. P. *J. Photochem. Photobiol., A* **2003**, 158, 183 (review).

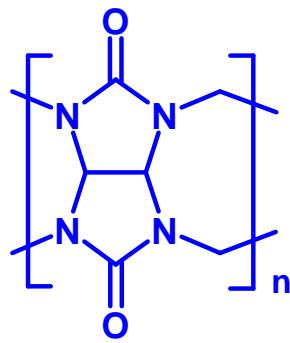
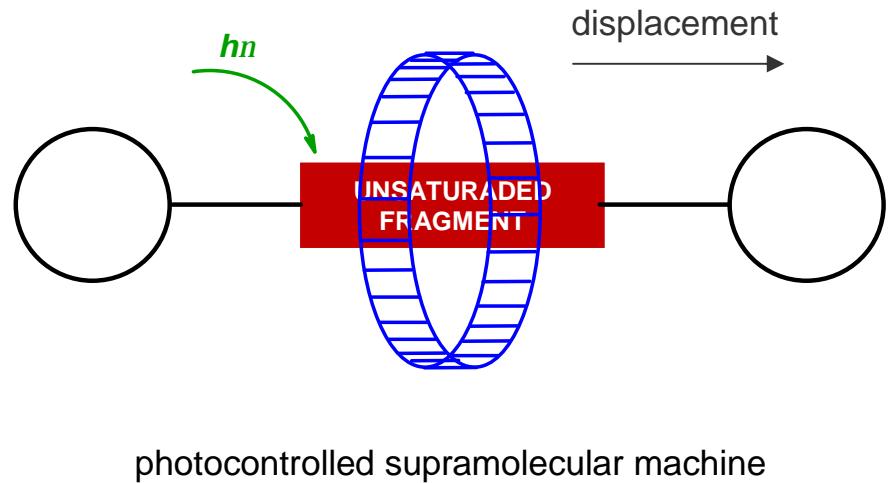
Crown-containing unsaturated compounds



$n = 1, 2$

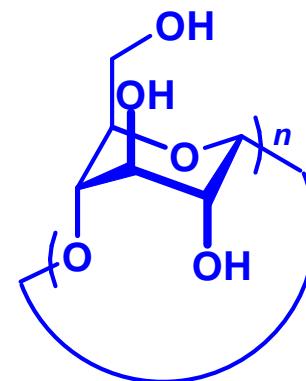
Gromov S. P., Alfimov M. V. *Russ. Chem. Bull.* **1997**, *46*, 611 (review);
Gromov S. P. *Russ. Chem. Bull.* **2008**, *57*, 1299 (review).

Photocontrolled supramolecular machines based on unsaturated compounds, cucurbiturils and cyclodextrins



cucurbiturils

$n = 6-8$



cyclodextrins

Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

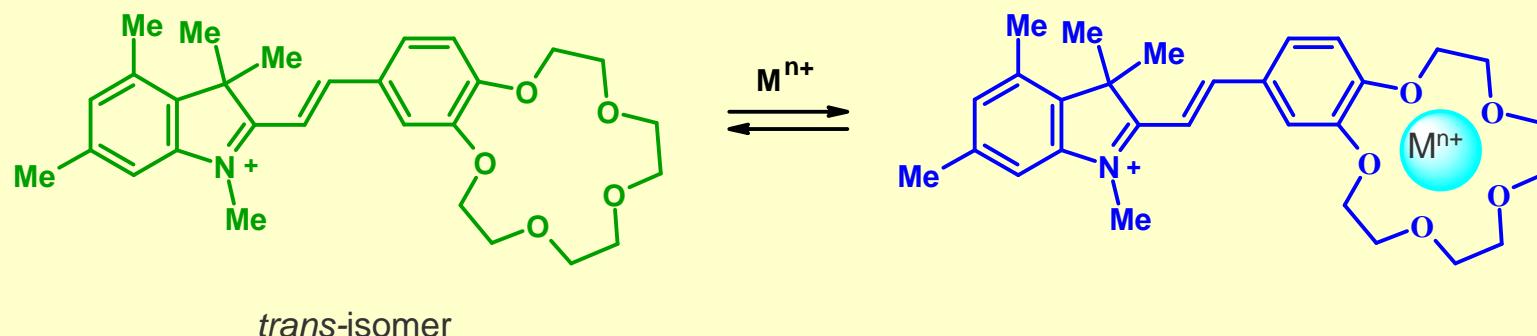
Gromov S. P. *Rev. J. Chem.* **2011**, 1, 1 (review)

Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, 84, 787 (review).

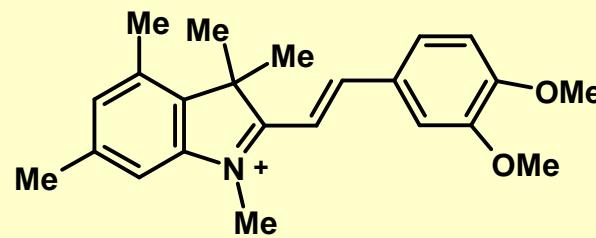
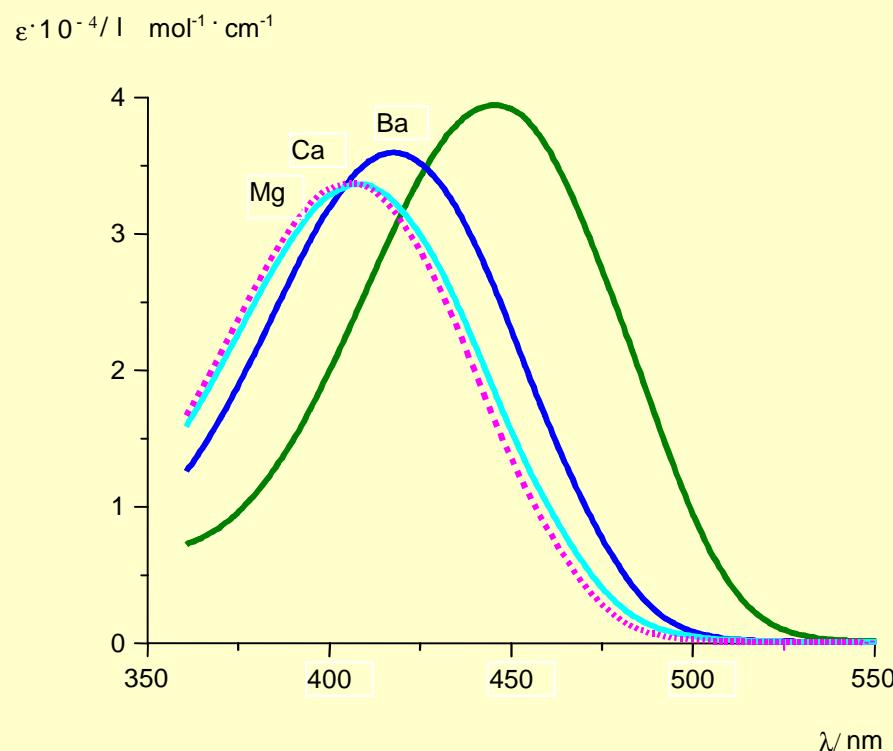
**Self-assembly
of photoswitchable supramolecular devices
with participation of metal cations**

Part I

Complex formation



trans-isomer

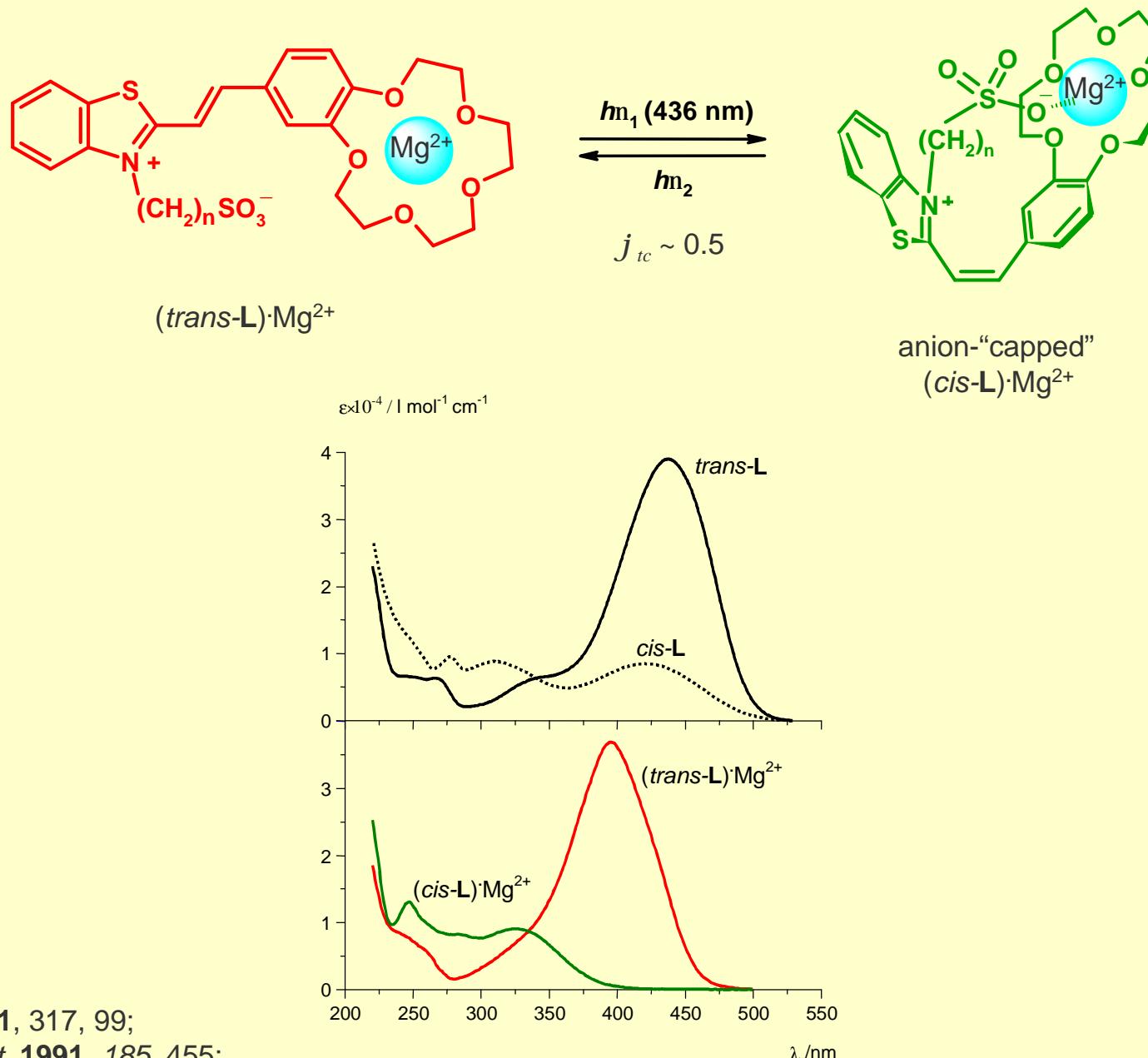


Dokl. Chem. 1990, 314, 279;

Ushakov E. N., Gromov S. P. et al. *Macrocycles*. 2010, 3, 189 (review)

J. Org. Chem. 2013, 78, 9834.

Photoswitchable supramolecular devices



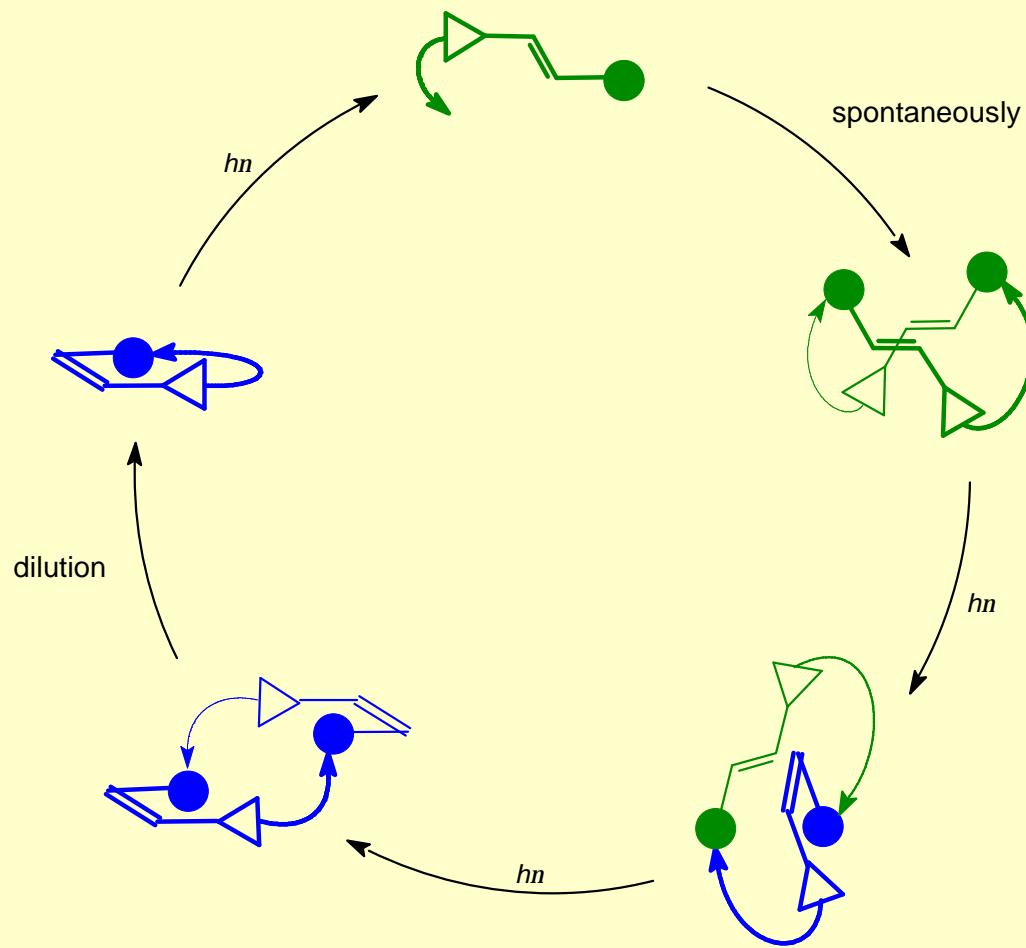
Dokl. Chem. 1991, 317, 99;

Chem. Phys. Lett. 1991, 185, 455;

J. Am. Chem. Soc. 1992, 114, 6381;

J. Am. Chem. Soc. 1999, 121, 4992.

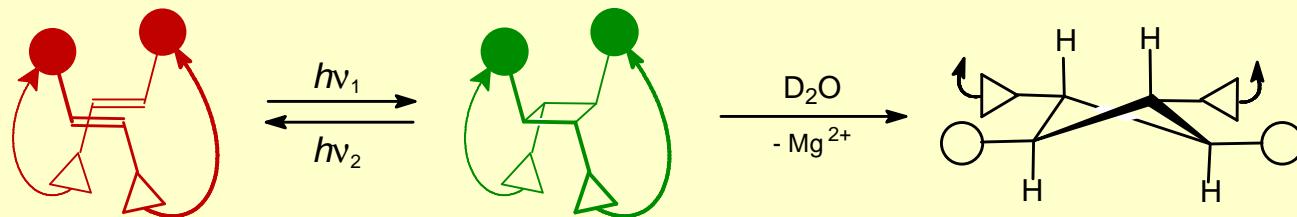
Photocycle of crown-containing styryl dyes



● - is the benzocrown compounds moiety with M^{2+} (Mg , Ca , Hg , Pb);

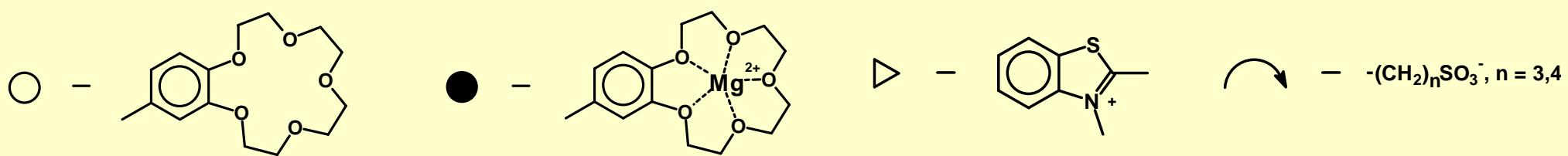
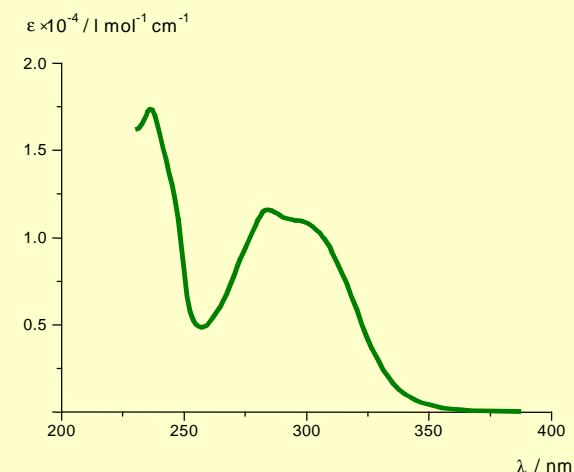
▷ - is the benzothiazolium moiety; ↗ - $(CH_2)_nSO_3^-$

Photoswitchable supramolecular devices



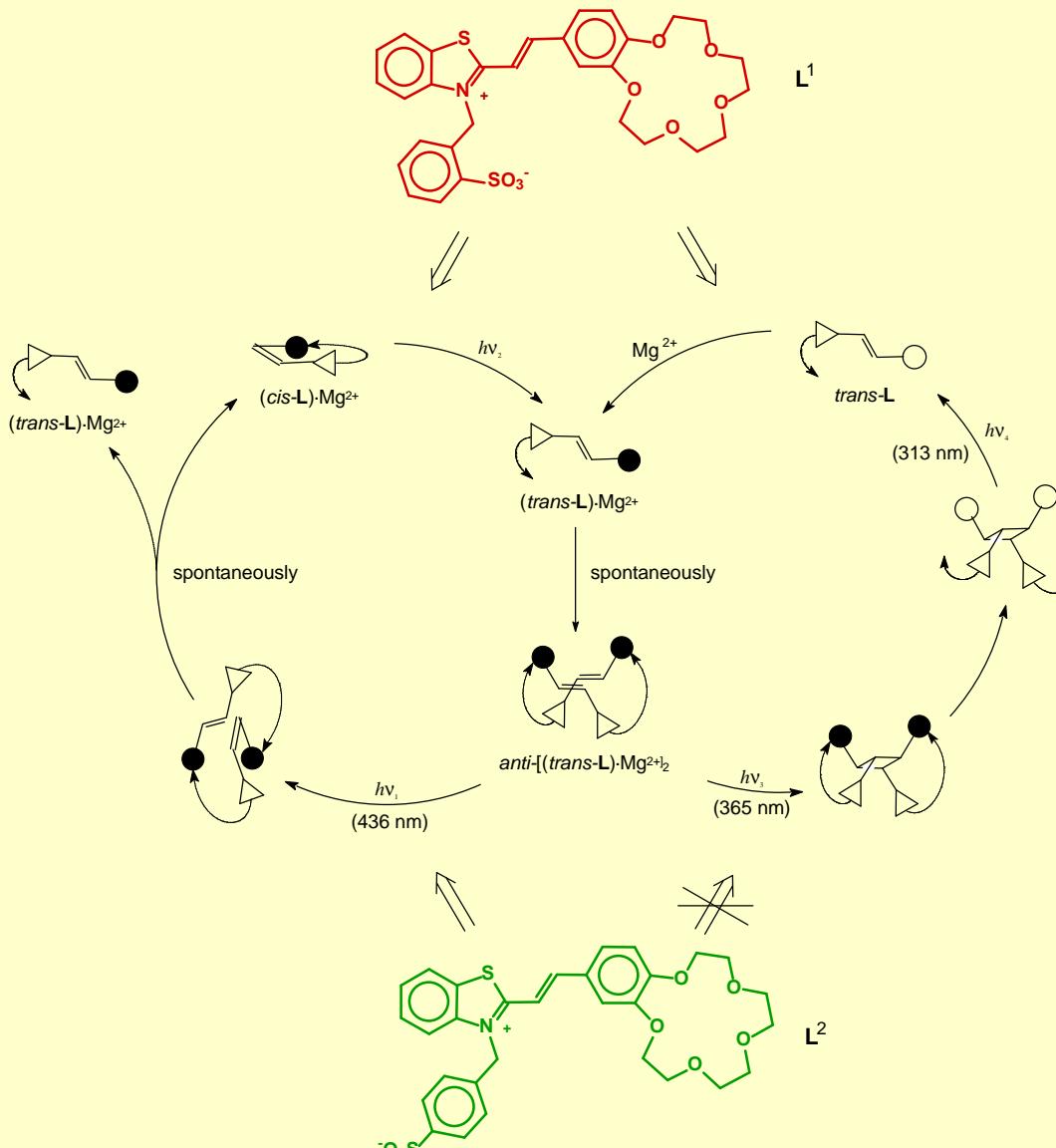
[2+2] Photocycloaddition of CSD

| | | | | | |
|---|-------------------|---------------------|---------------------|---------------------|-------------------|
| $C_L, / \text{mol} \cdot \text{l}^{-1}$ | $5 \cdot 10^{-6}$ | $2.4 \cdot 10^{-5}$ | $4.5 \cdot 10^{-5}$ | $2.1 \cdot 10^{-4}$ | $2 \cdot 10^{-3}$ |
| F | 0.0022 | 0.0043 | 0.0052 | 0.0051 | 0.0055 |



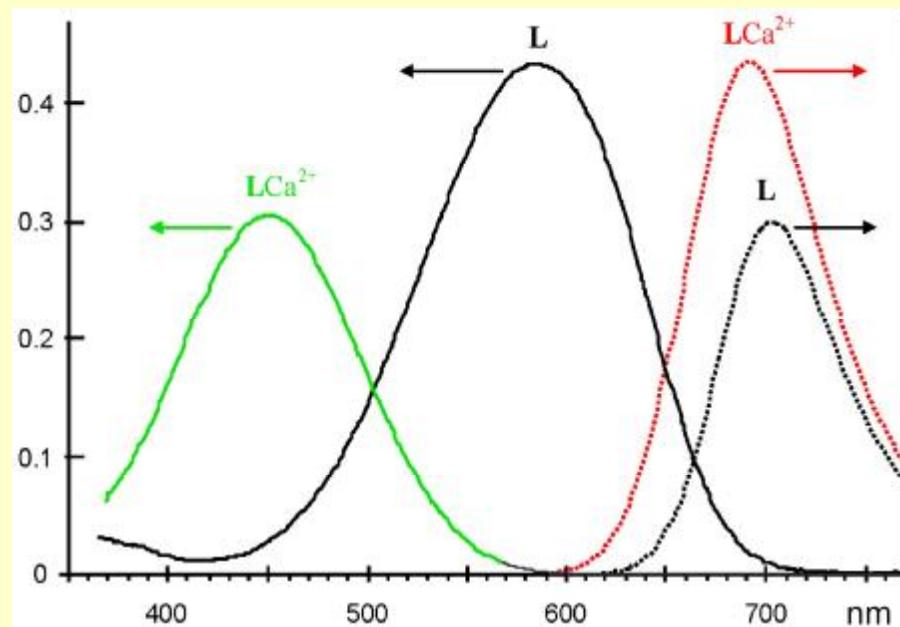
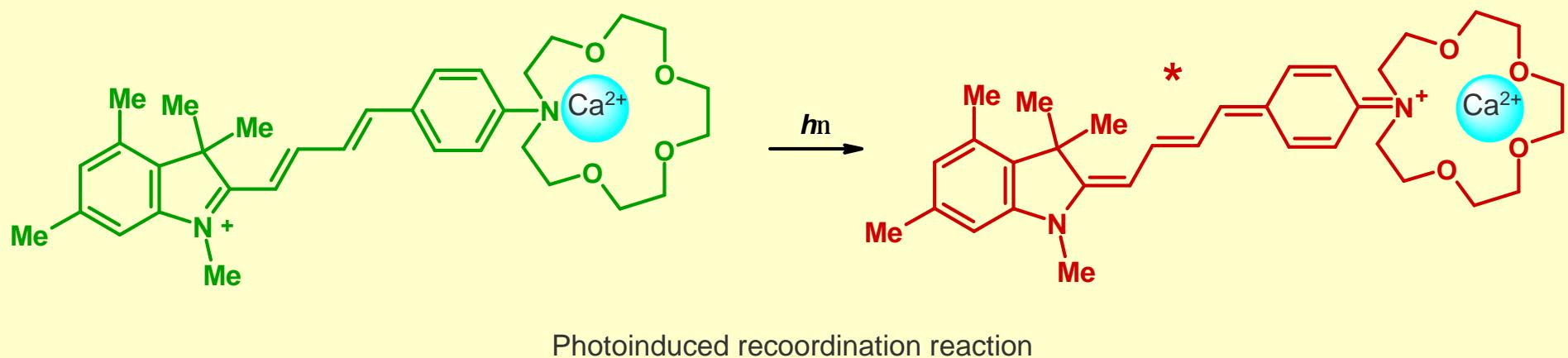
J. Am. Chem. Soc. **1992**, *114*, 6381;
Russ. Chem. Bull. **1993**, *42*, 1385;
J. Chem. Soc., Perkin Trans. 2 **1999**, 601;
J. Org. Chem. **2003**, *68*, 6115.

[2+2] PHOTOCYCLOADDITION OF MULTIPHOTOCROMIC CSD



| CSD | R, Å° | F | log K ₁ |
|-------|-------|-------|--------------------|
| L^1 | 6.7 | 0.018 | 7.3 |
| L^2 | 9.9 | --- | 10.0 |

Photoswitchable supramolecular device

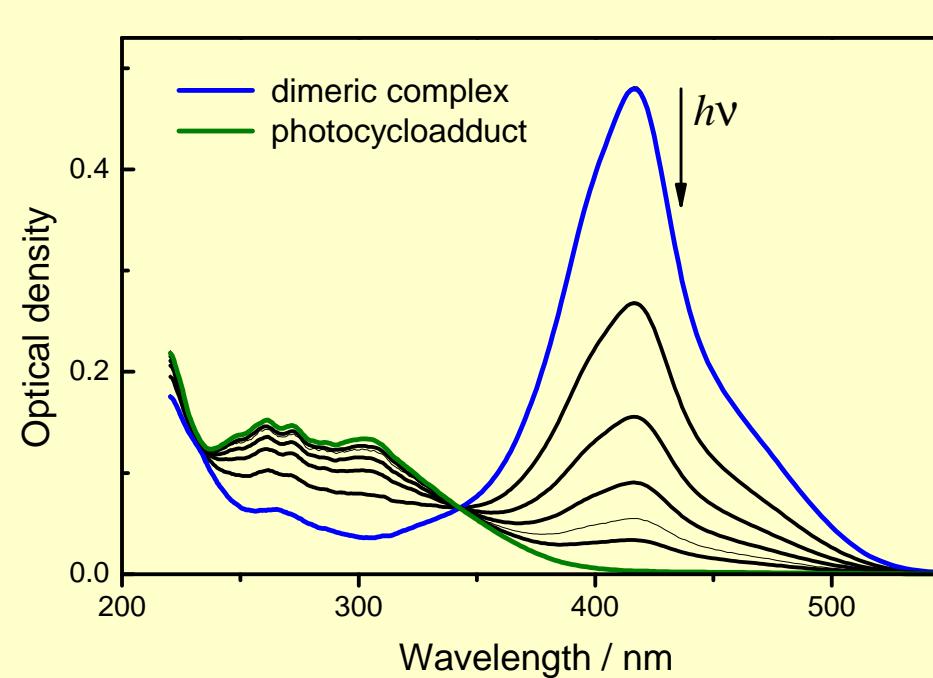
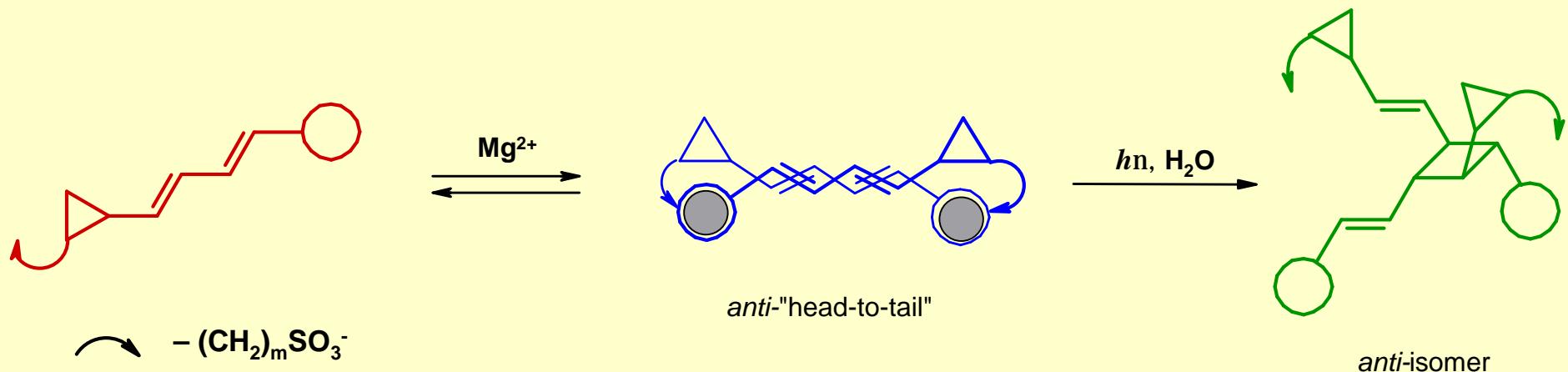


Russ. Chem. Bull. 1999, 48, 525;

J. Fluor. 1999, 9, 33;

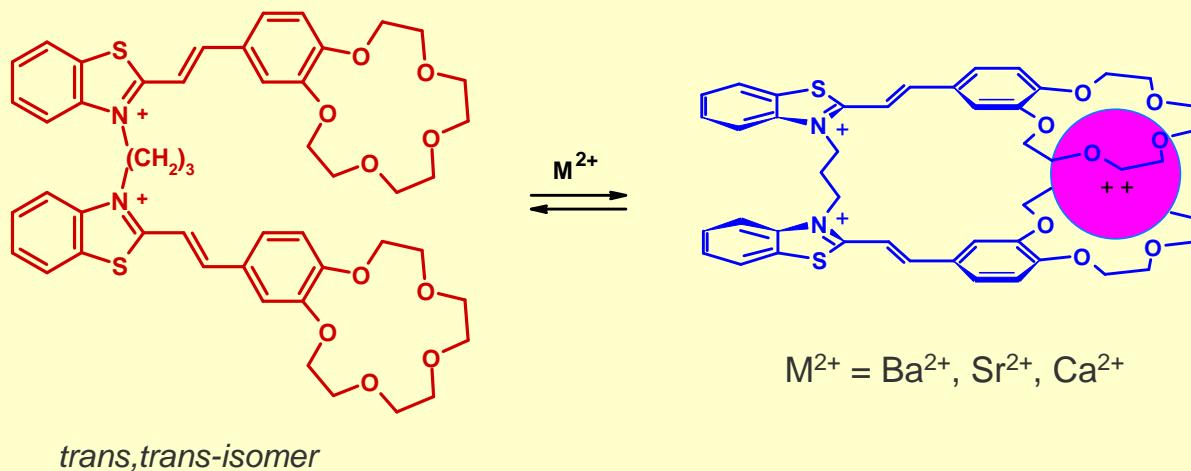
Rusalov M. V., Gromov S. P. et al. Russ. Chem. Rev. 2010, 79, 1193 (review).

[2+2] PHOTOCYCLOADDITION OF CBD

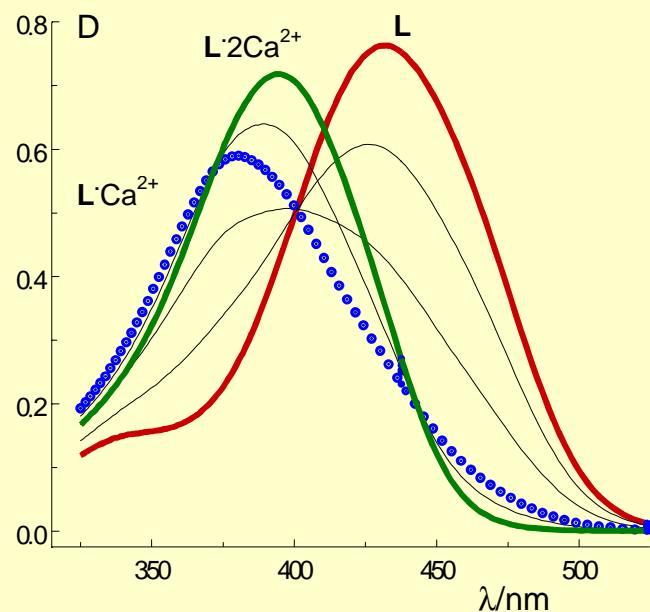


$F_{\text{PCA}} = 0.35$

Self-assembly of sandwich complexes



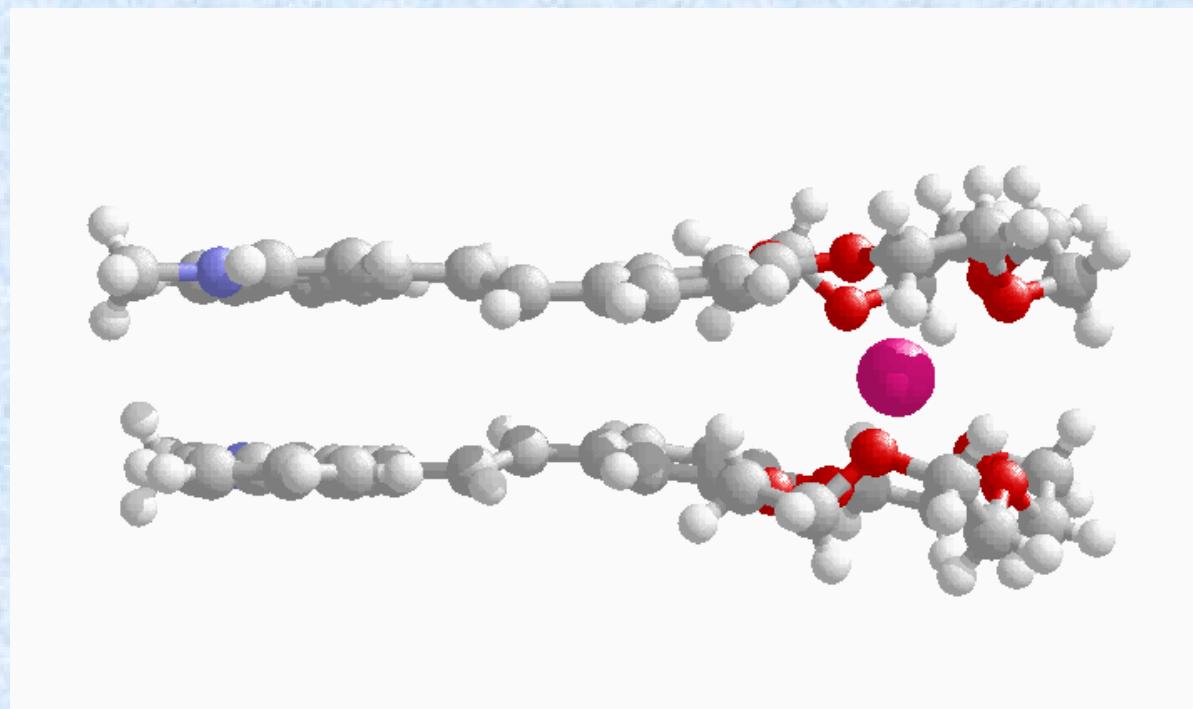
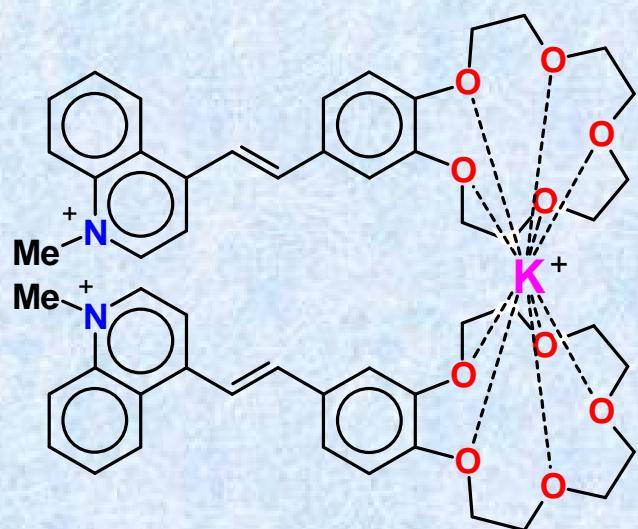
trans,trans-isomer



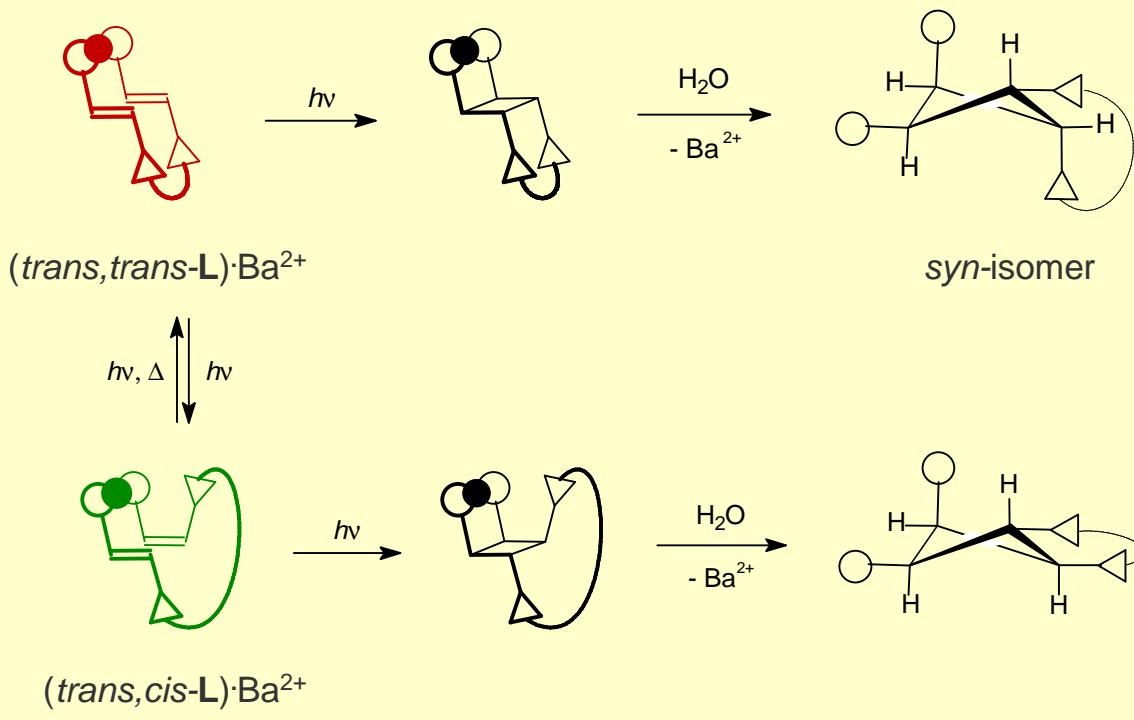
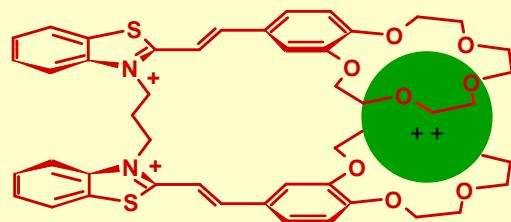
| Complex | $\log K_1$ | λ_{LM} , nm | $\lambda_L - \lambda_{LM}$, nm |
|----------------------------|------------|---------------------|---------------------------------|
| $L \cdot Ba^{2+}$ | 8.0 | 390 | 42 |
| Monomer · Ba ²⁺ | 4.39 | 402 | 28 |

J. Chem. Soc., Perkin Trans. 2. 1999, 1323;
J. Phys. Chem. A. 1999, 103, 11188;
RF patent 2389745 2010.

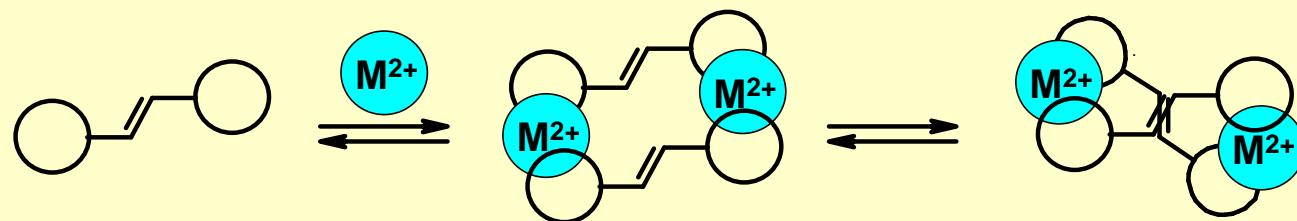
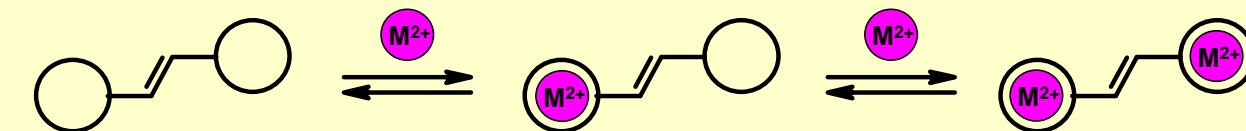
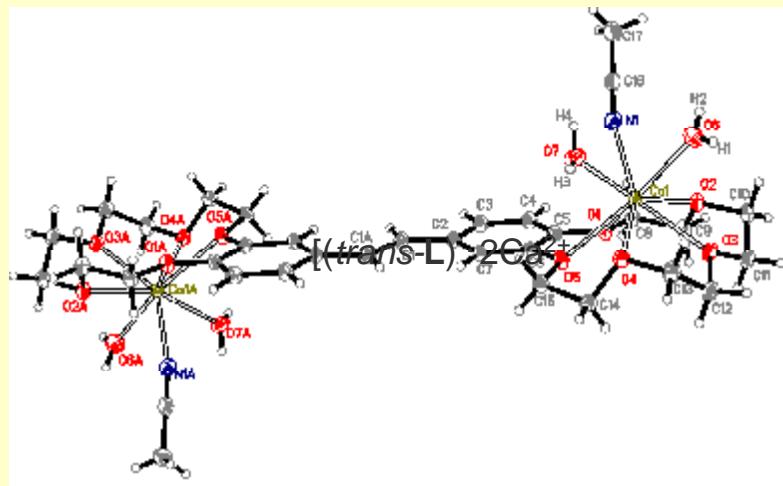
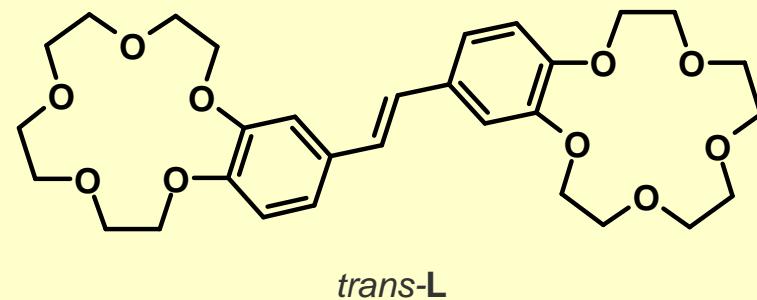
X-ray structure determination of sandwich complex



Intramolecular [2+2] photocycloaddition of bisCSD



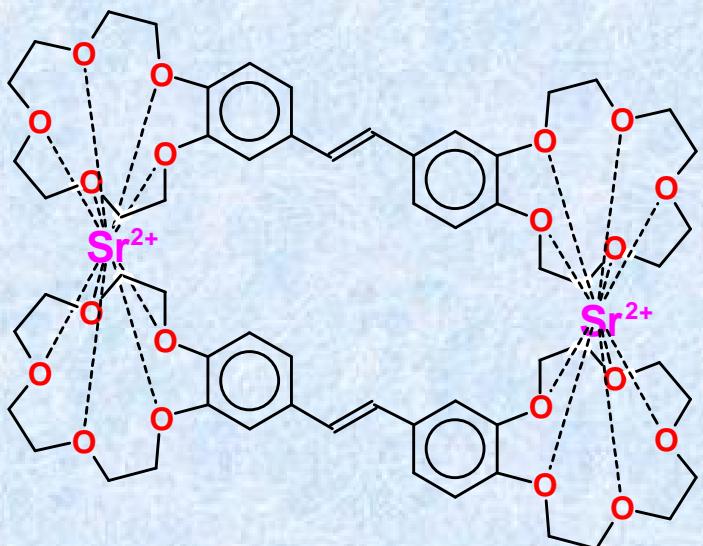
Complex formation of bisCS



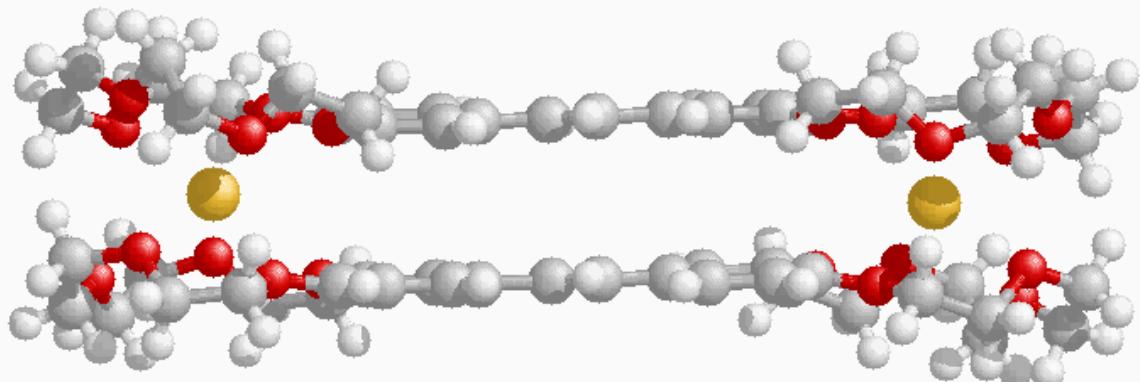
M^{2+} = Mg^{2+}, Ca^{2+}

M^{2+} = Sr^{2+}, Ba^{2+}

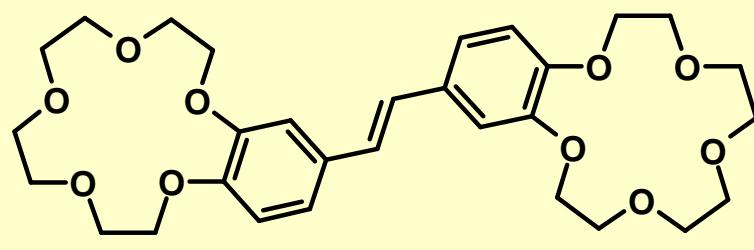
X-ray structure determination of double sandwich complex



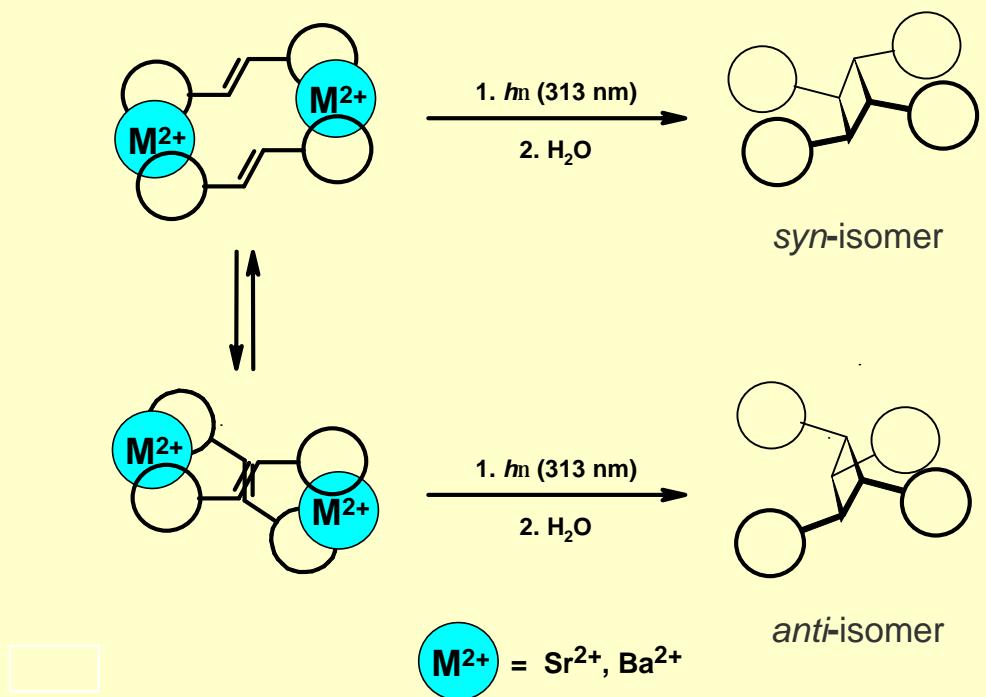
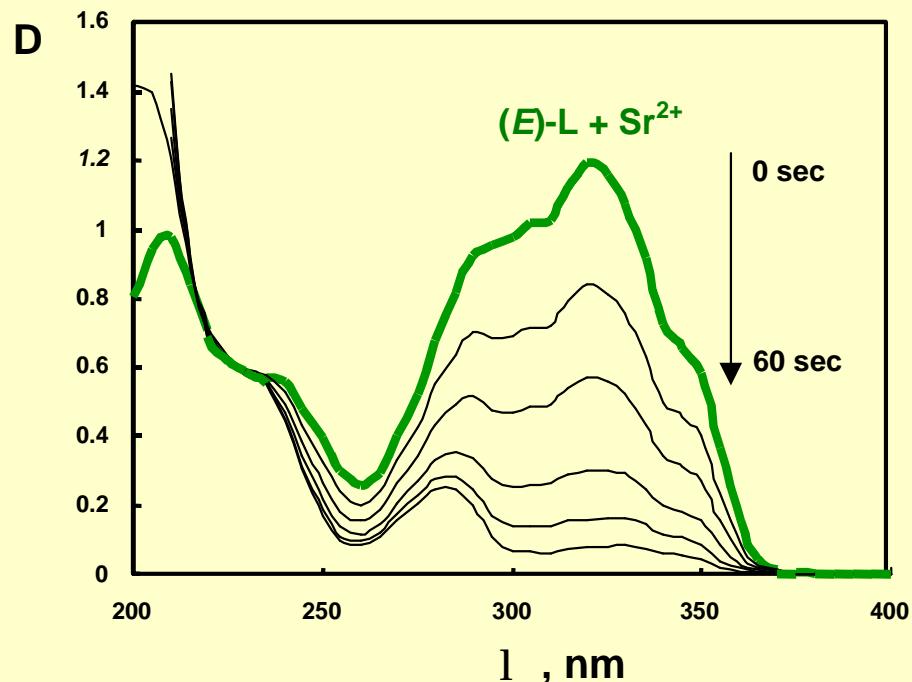
$2(\text{trans-L}) \cdot 2\text{Sr}^{2+}$



[2+2] Photocycloaddition of bisCS



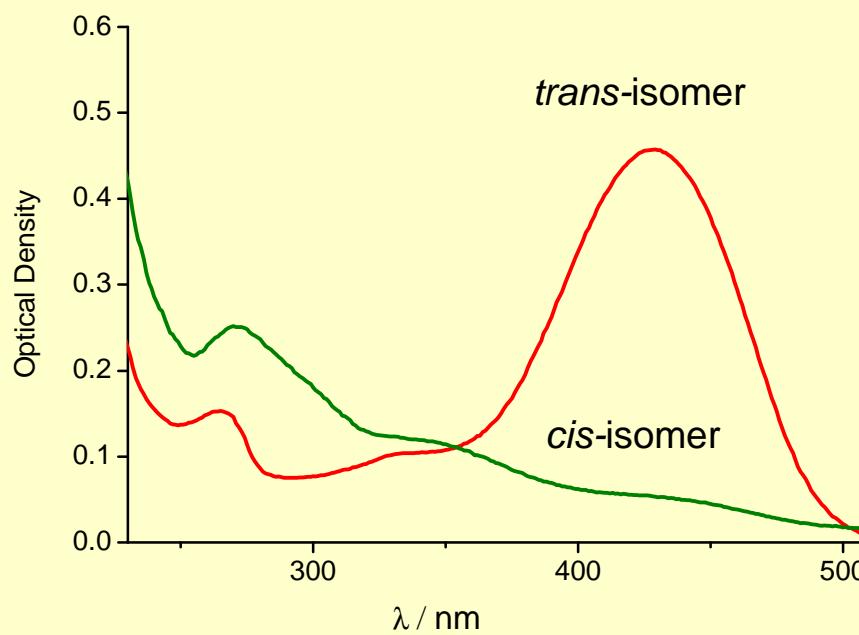
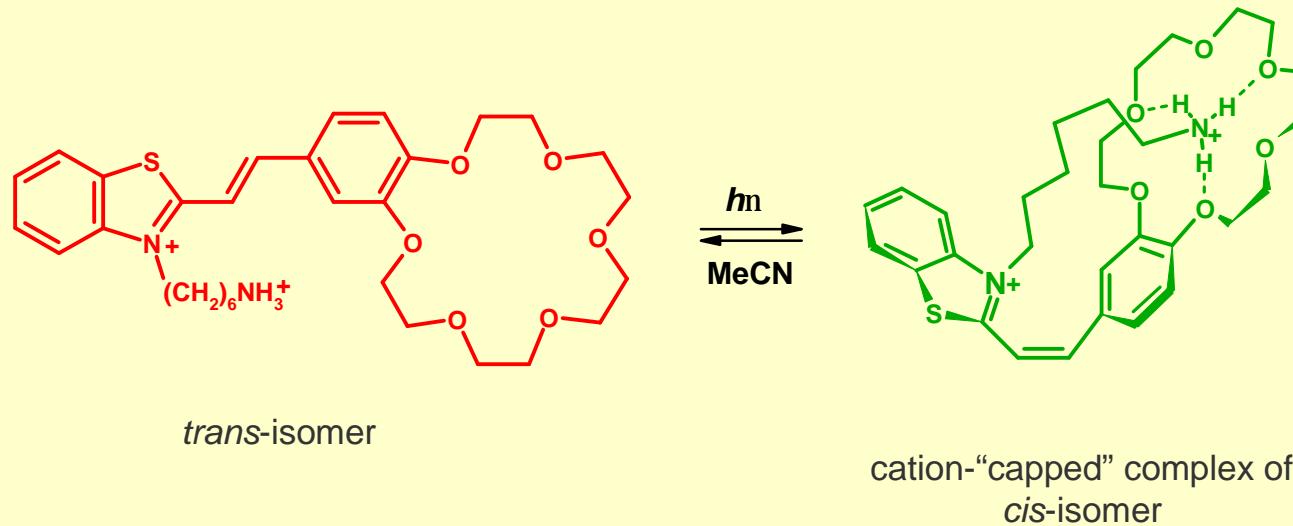
trans-L



**Self-assembly
of photoswitchable supramolecular devices
with participation of hydrogen bonds**

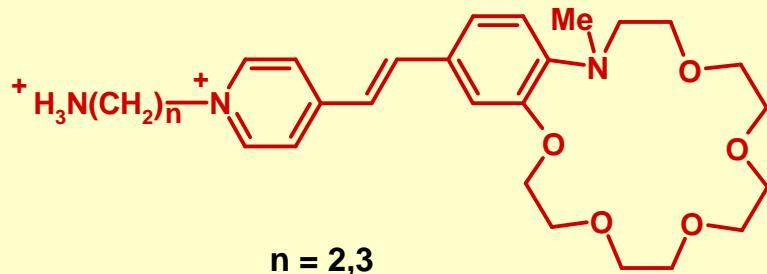
Part II

Intramolecular complexation of *cis*-isomers

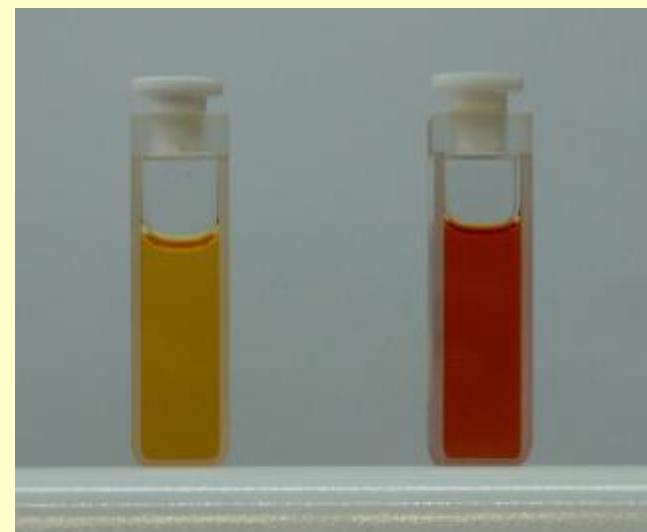
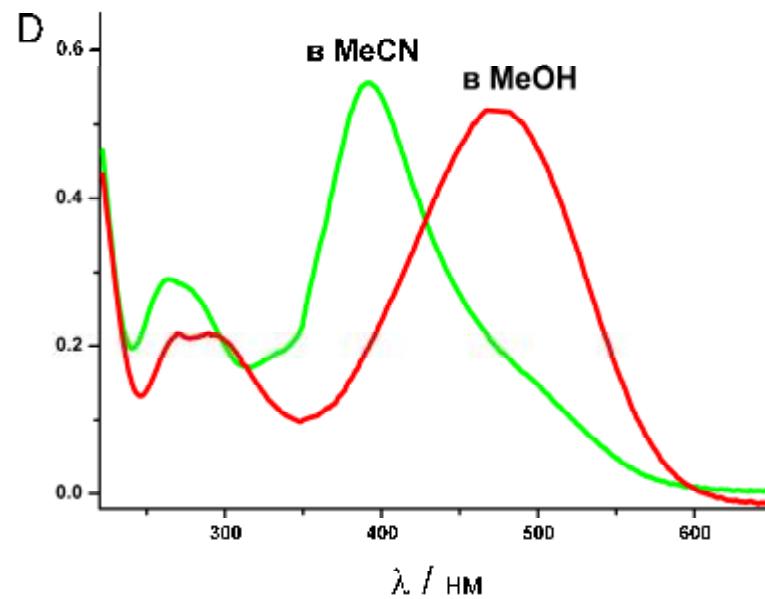
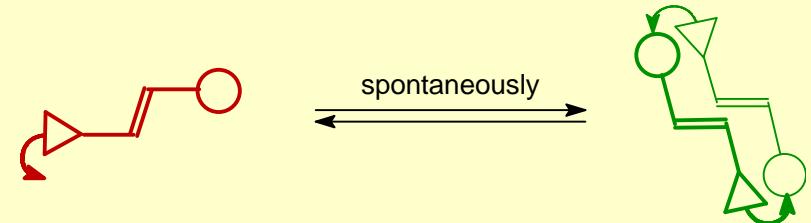


Mendeleev Commun. **2007**, *17*, 264;
J. Mol. Structure. **2009**, *935*, 136.

Dimerization of CSD



n = 2,3



in MeCN

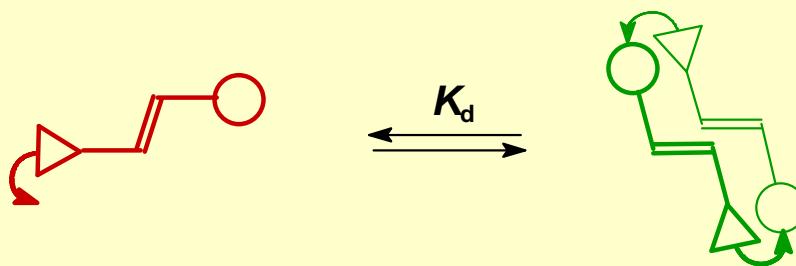
in MeOH

RF patent 2278134 2006;

J. Org. Chem. 2014, 79, 11416;

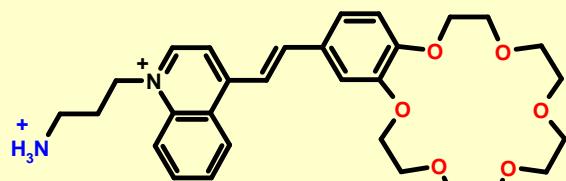
J. Phys. Chem. A 2015, 119, 13025.

DIMERIZATION

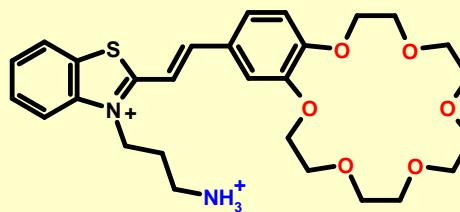


$\log K_d$

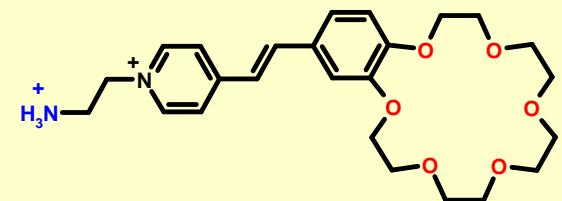
$\log K_d$



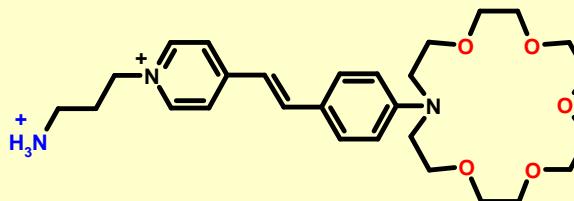
8.03



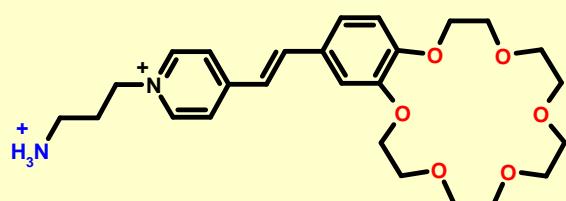
5.87



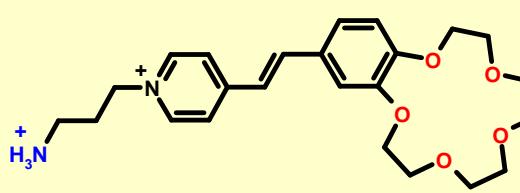
7.90



3.61



7.12

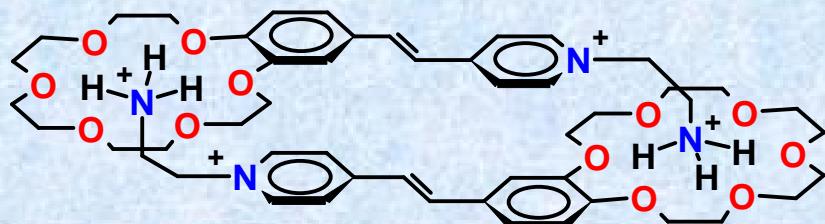


2.44

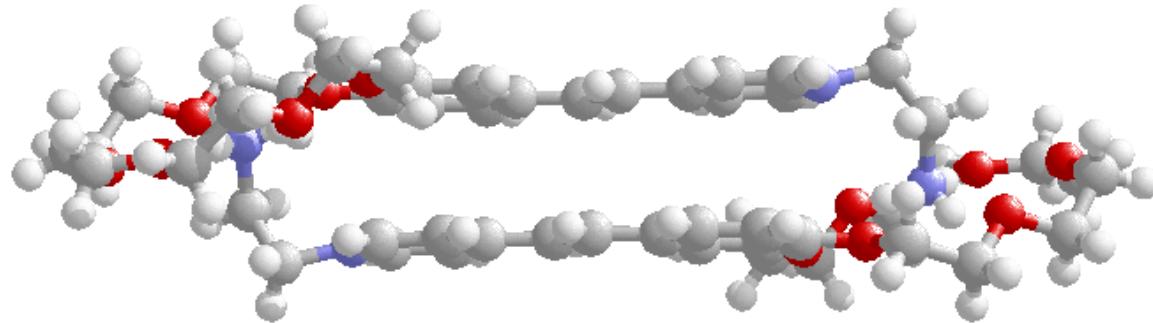
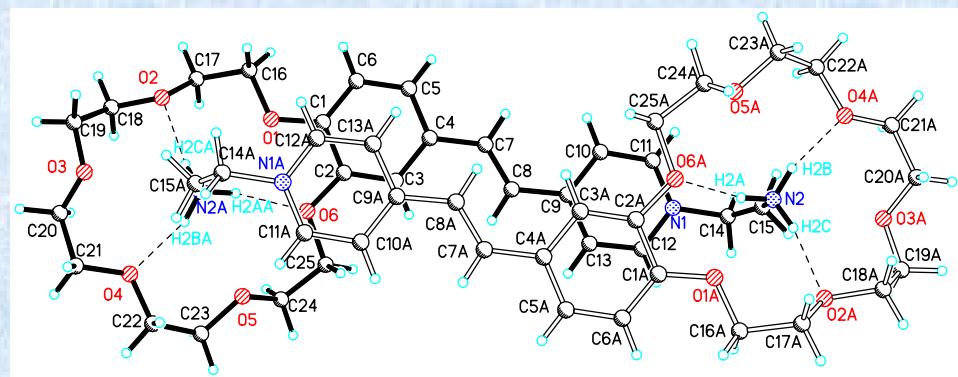
in CD_3CN

Russ. Chem. Bull. 2009, 58, 1211;
J. Org. Chem. 2014, 79, 11416;
J. Phys. Chem. A 2015, 119, 13025.

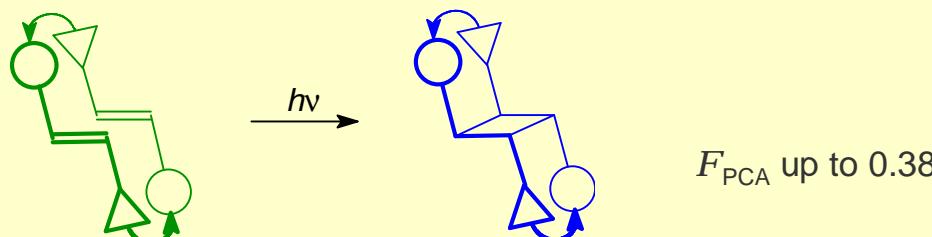
X-ray structure determination of dimeric complex



syn-'head-to-tail' dimeric complex

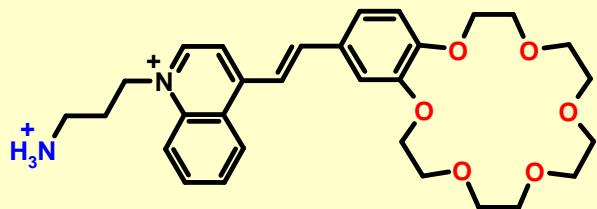


[2+2] Photocycloaddition of CSD

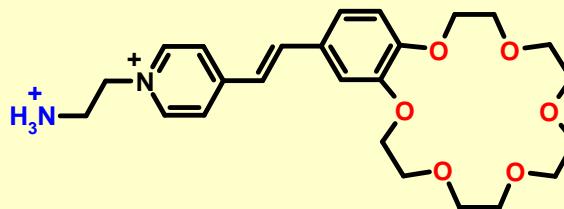


Yield, %

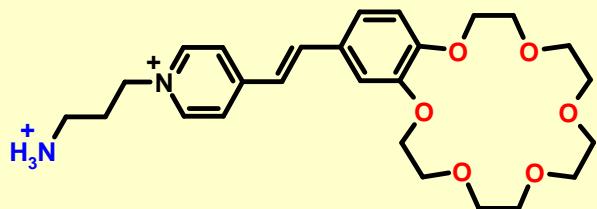
Yield, %



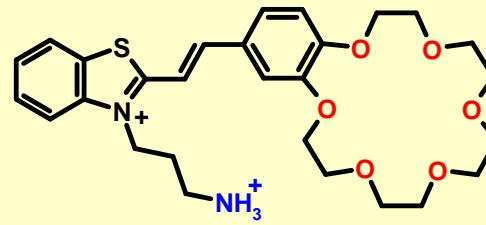
100



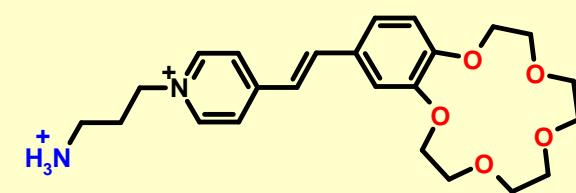
33



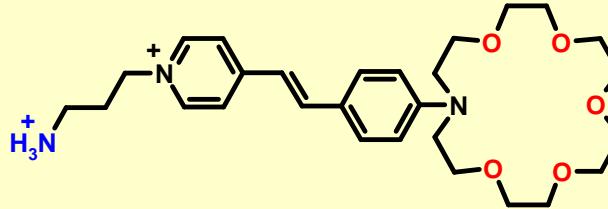
100



0



40

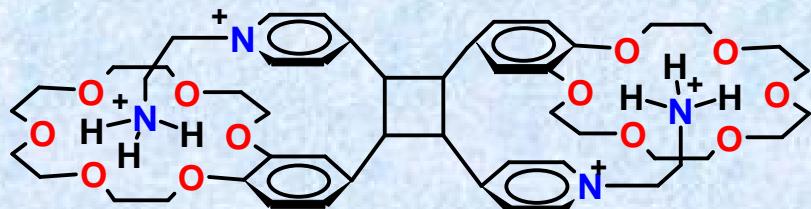


0

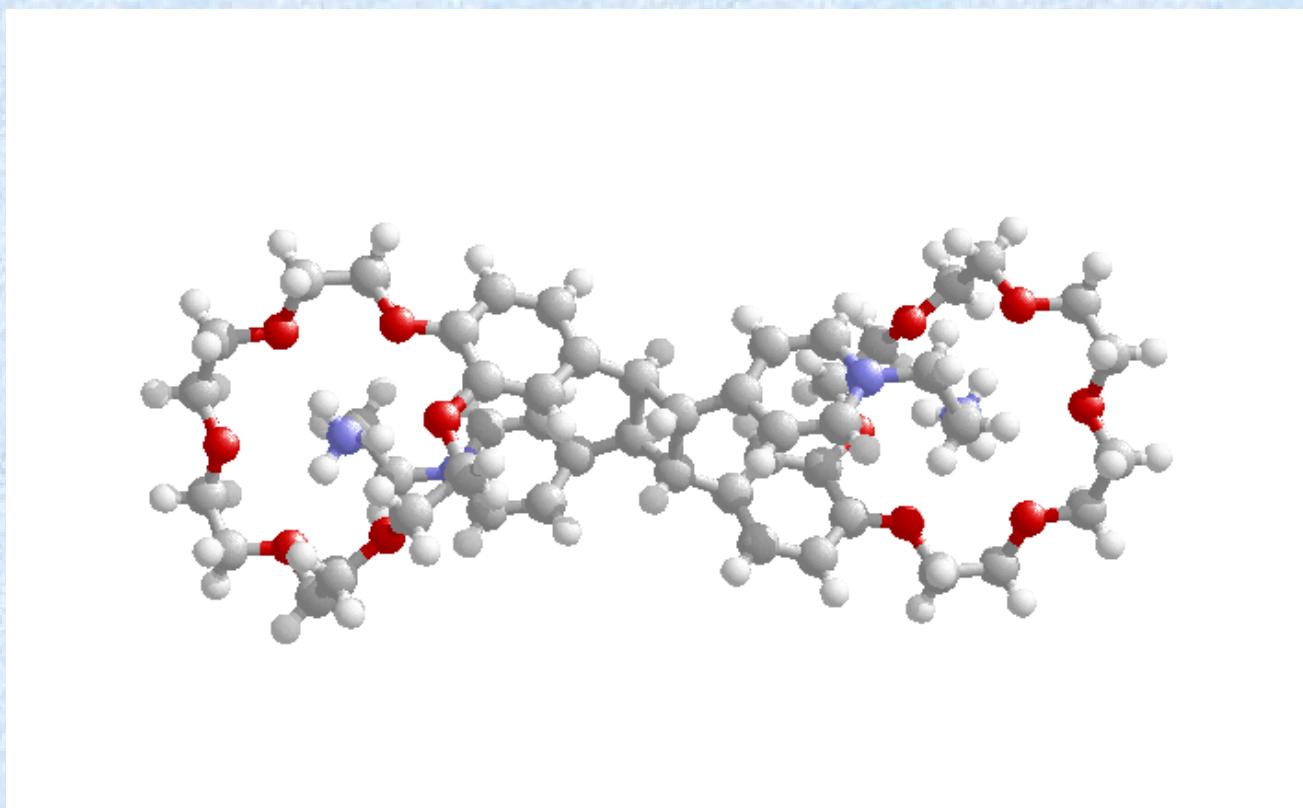
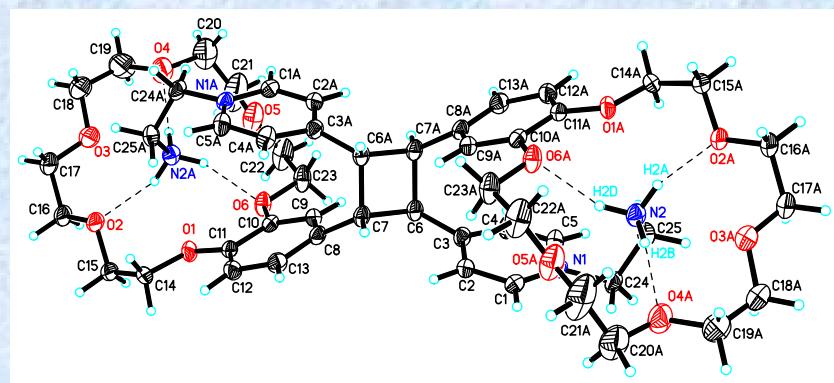
RF patent 2278134 2006;
Russ. Chem. Bull. 2009, 58, 1211;
J. Org. Chem. 2014, 79, 11416;
J. Phys. Chem. A 2015, 119, 13025.

In MeCN, irradiation time, 4 h

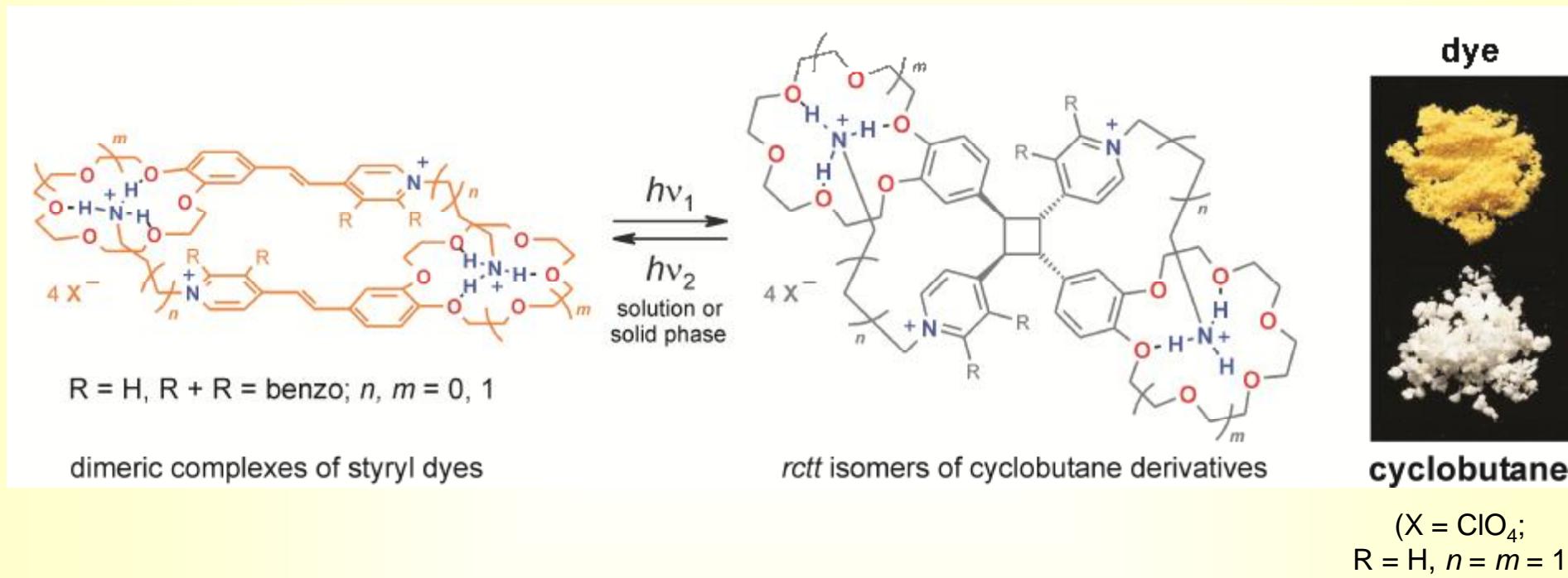
X-ray structure determination of cyclobutane



syn-cyclobutane

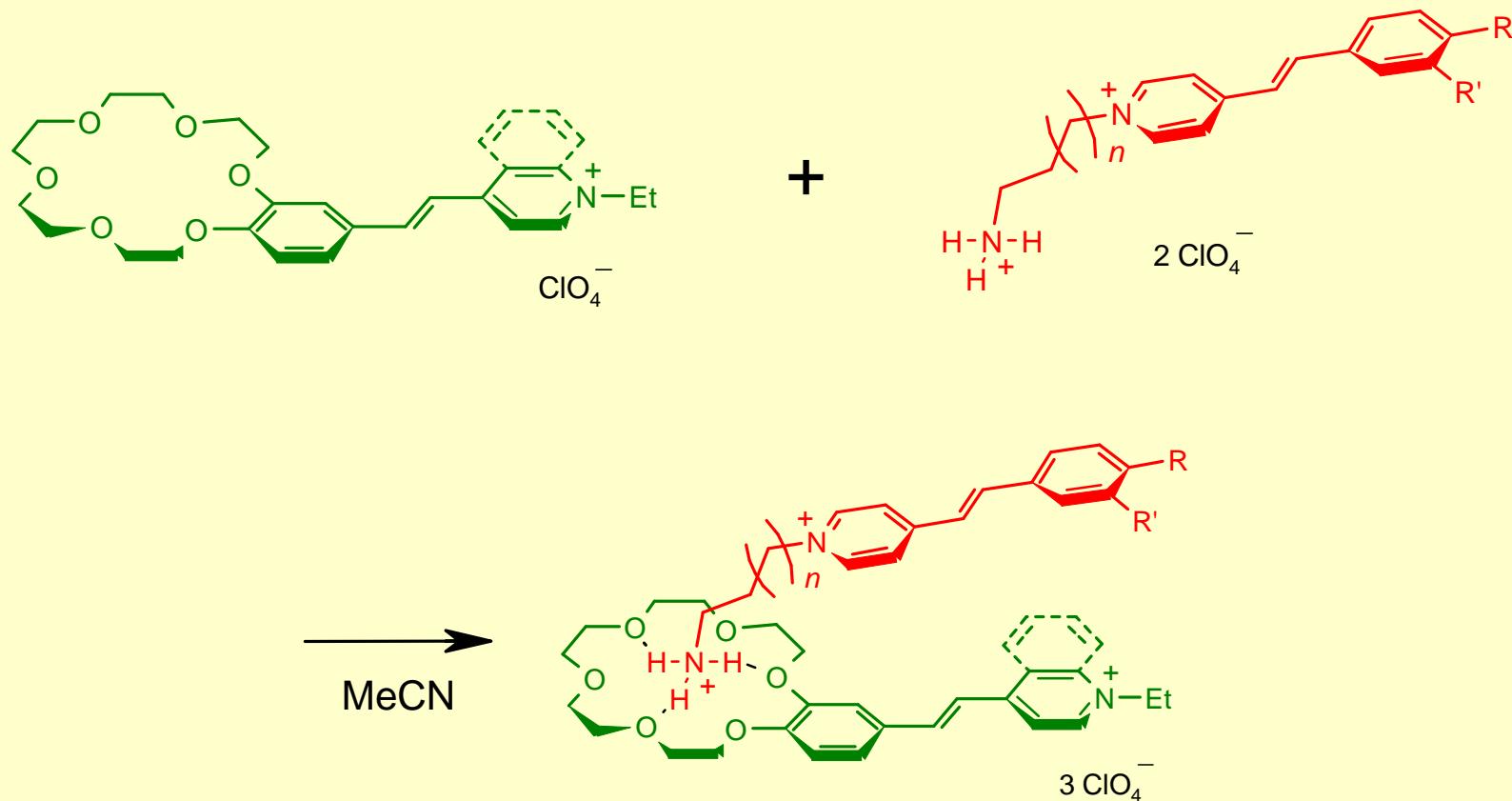


Supramolecular photoswitches based on ammonioalkyl derivatives of crown-ether styryl dyes



Found property provides grounds for believing that the crystals of these photoactive supramolecular systems could be used for data recording and storage.

Formation of pseudodimeric complexes



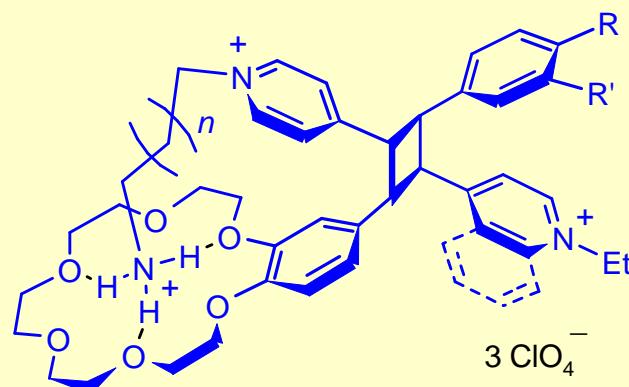
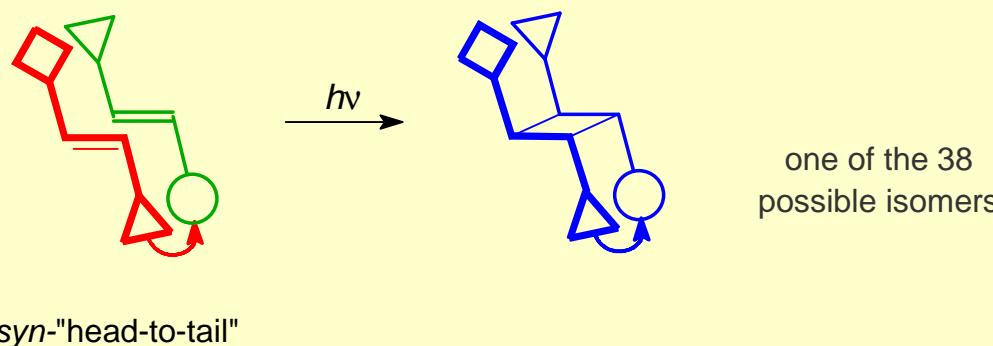
$\text{R}, \text{R}' = \text{H}, \text{OMe}, \text{SMe}, \text{NMe}_2, \text{NO}_2, \text{Cl}$

$n = 0, 1, 3$

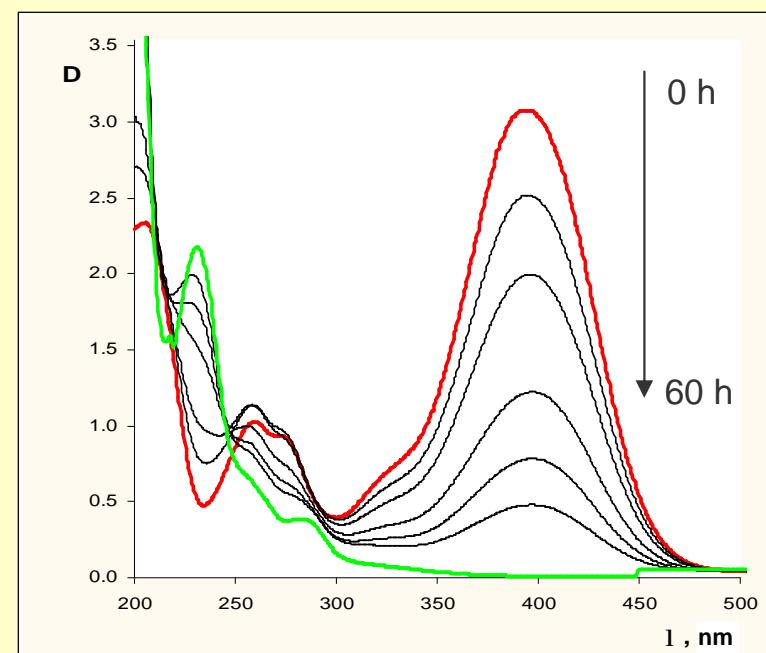
$\log K = 3.1 - 3.7$

Mendeleev Commun., 2007, 17, 29;
Russ. Chem. Bull. 2009, 58, 1955;
New. J. Chem. 2016, 40, 7542.

[2+2] cross-Photocycloaddition

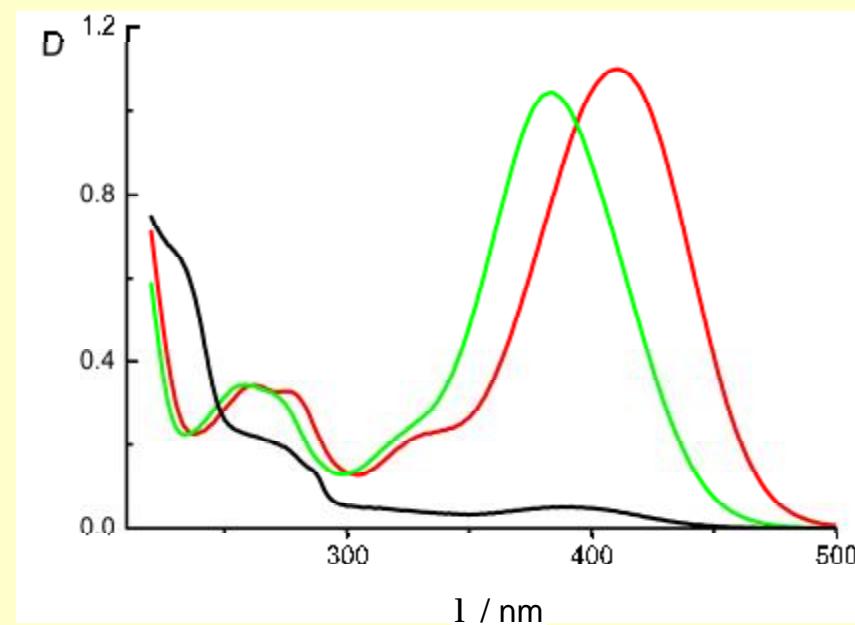
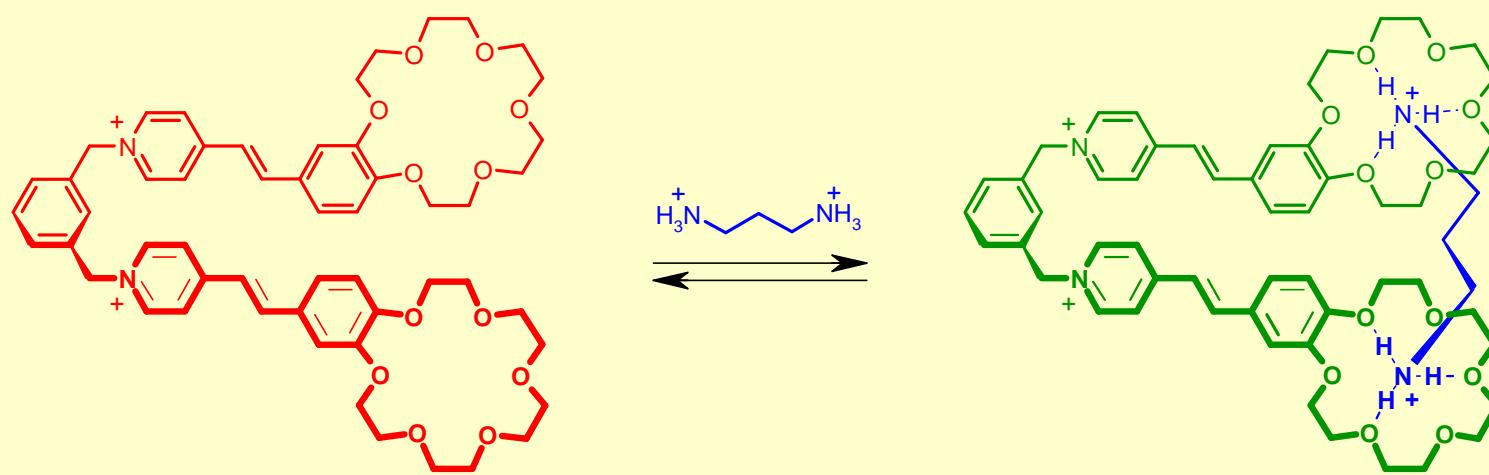


rctt isomers

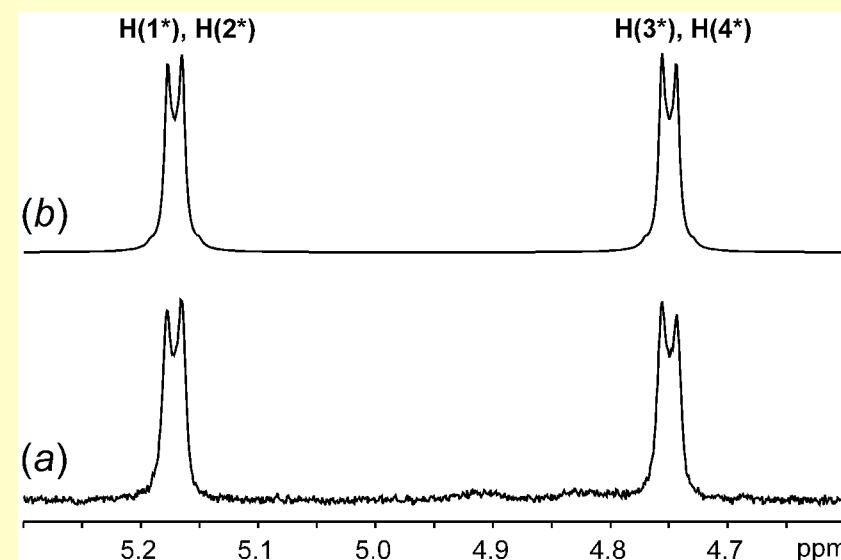
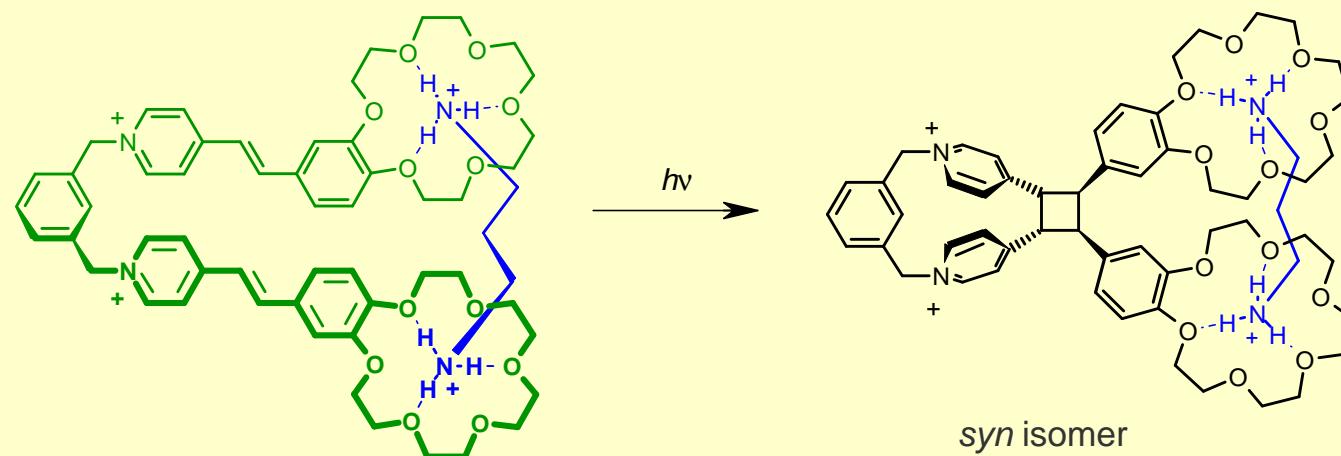


Mendeleev Commun., 2007, 17, 29;
Russ. Chem. Bull. 2009, 58, 1955;
RF patent 2383571 2010;
New. J. Chem. 2016, 40, 7542.

FORMATION OF PSEUDOSANDWICH COMPLEXES

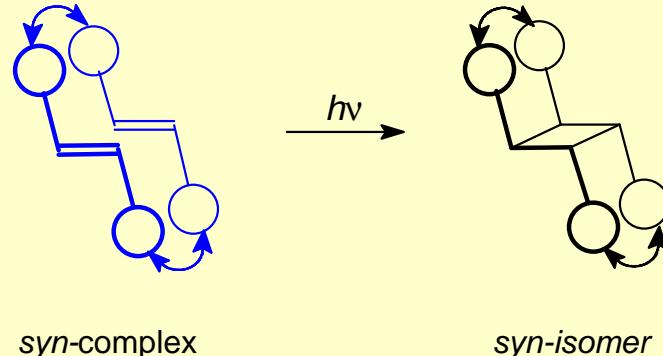


Intramolecular [2+2] photocycloaddition of bisCSD

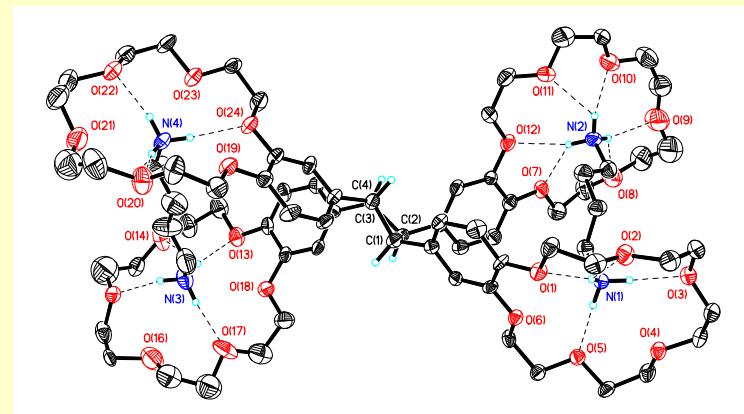
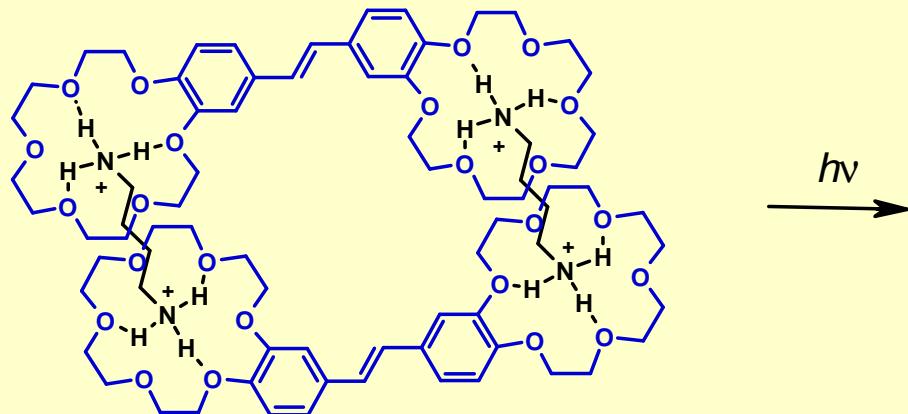
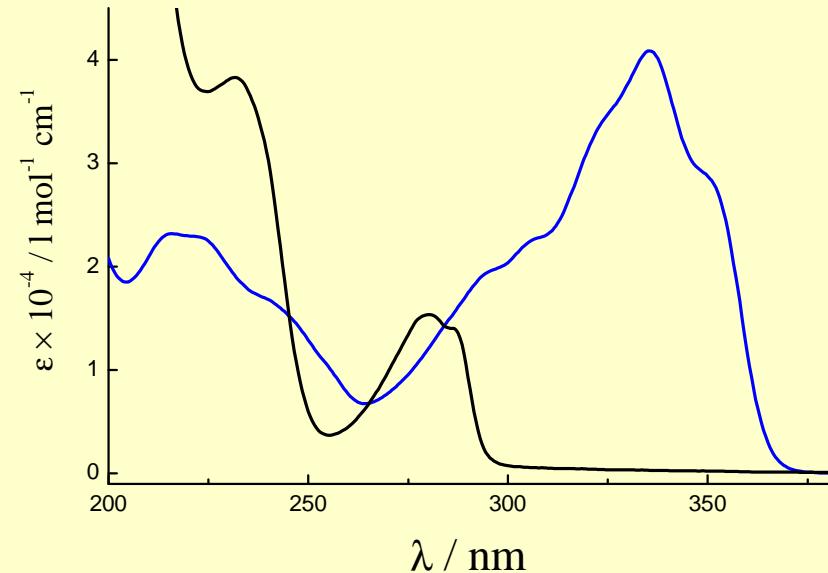
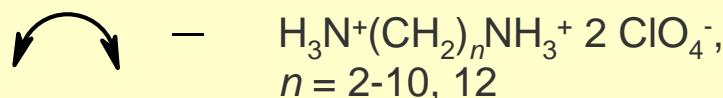


(a) ^1H NMR spectrum of the cyclobutane protons and (b) its best fit to an AA'BB' spin system.

Formation of bispseudosandwich complexes and [2+2] Photocycloaddition



F_{PCA} up to 0.27



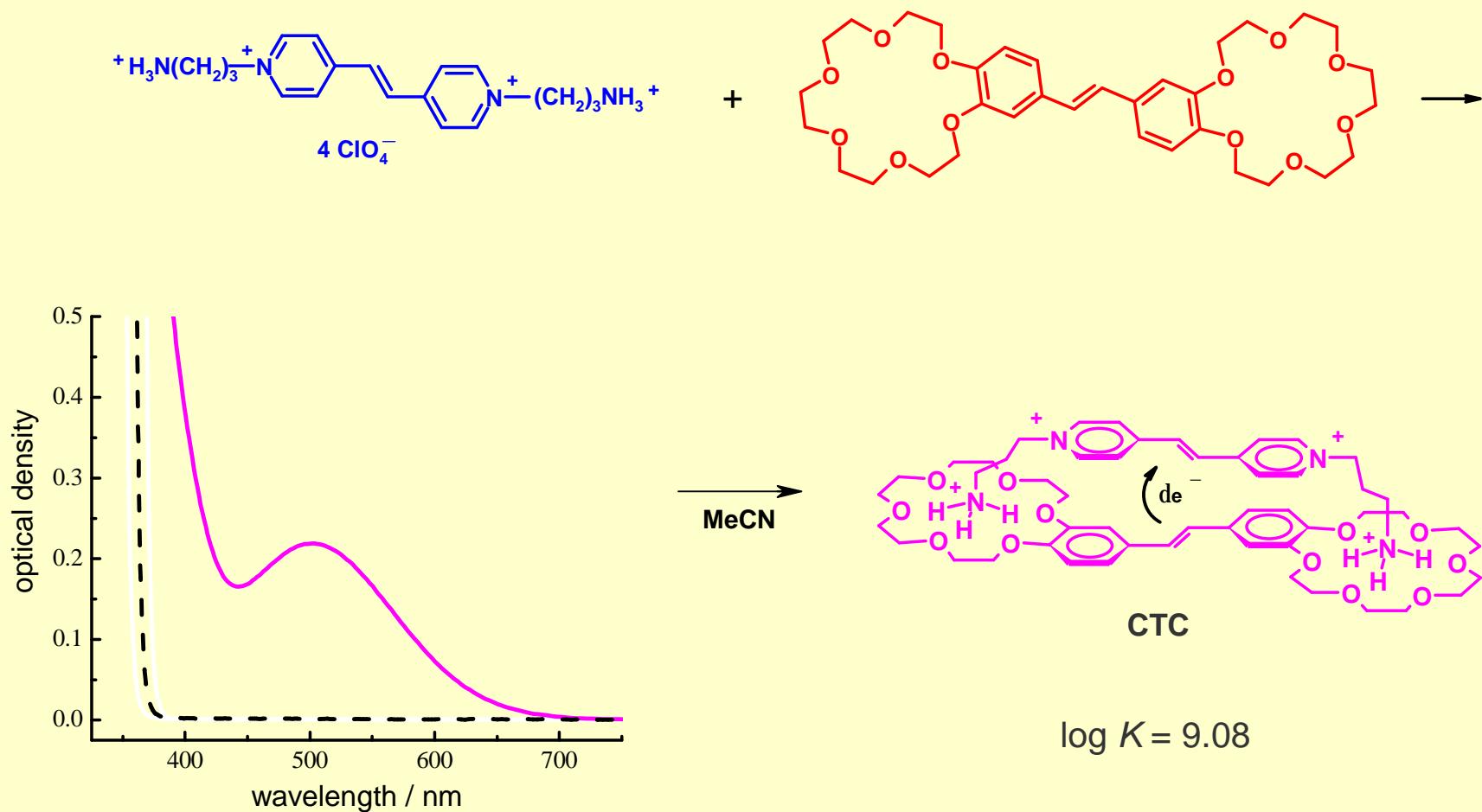
syn-isomer

Russ. Chem. Bull. 2009, 58, 108;

New J. Chem. 2011, 35, 724;

J. Photochem. Photobiol. A. 2017, 340, 80;

Formation of Charge Transfer Complex of bisCS

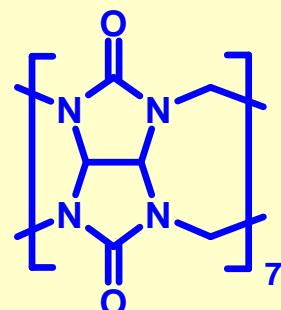


Org. Lett. 1999, 1, 1697 ;
New. J. Chem. 2005, 29, 881;
J. Org. Chem. 2011, 76, 6768;
Photochem. Photobiol. Sci. 2017, 16, 1801.

Self-assembly of photocontrolled supramolecular machines

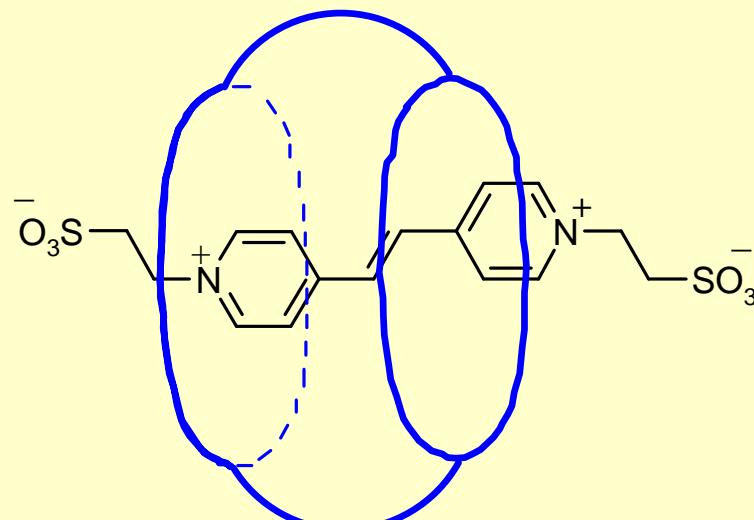
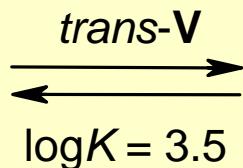
Part III

PSEUDOROTAXANE COMPLEXES OF CUCURBITURILS



CB[7]

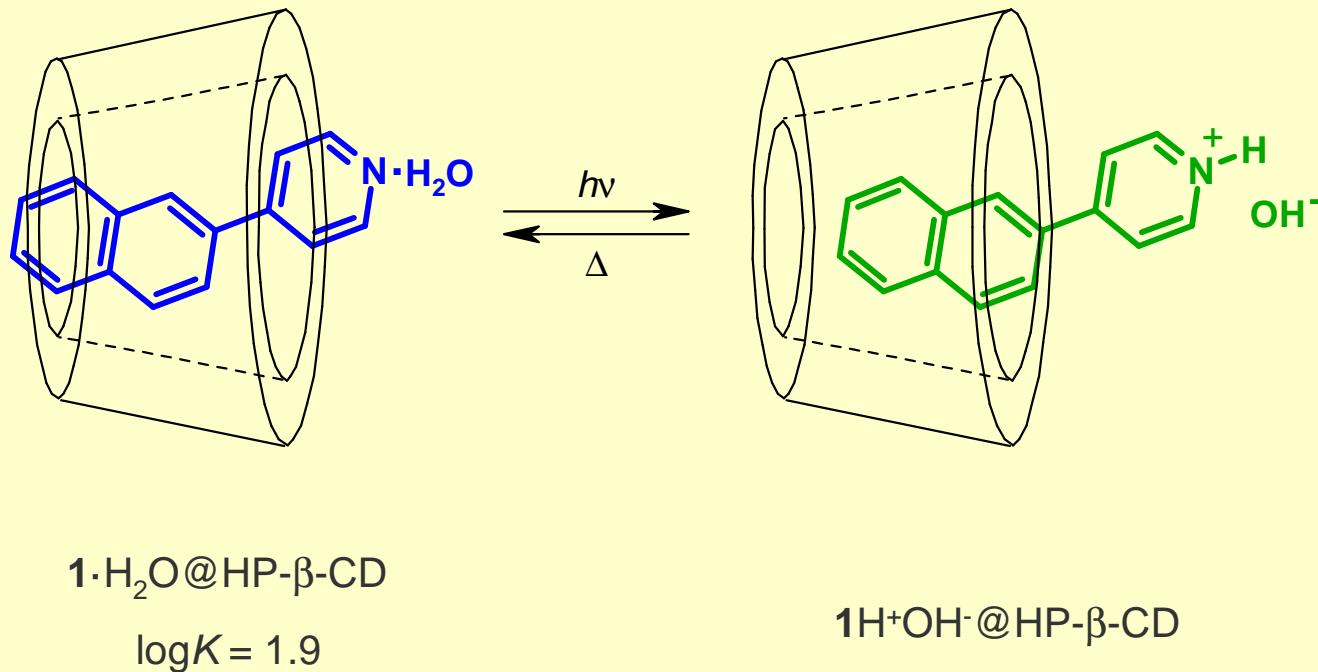
cucurbit[n]urils



trans-V@CB[7]

Russian Nanotechnologies **2007**, *2*, 56;
J. Mol. Struct. **2011**, *989*, 114;
Chem. Phys. Lett. **2014**, *610-611*, 91;
J. Photochem. Photobio. A **2018**, *353*, 34.

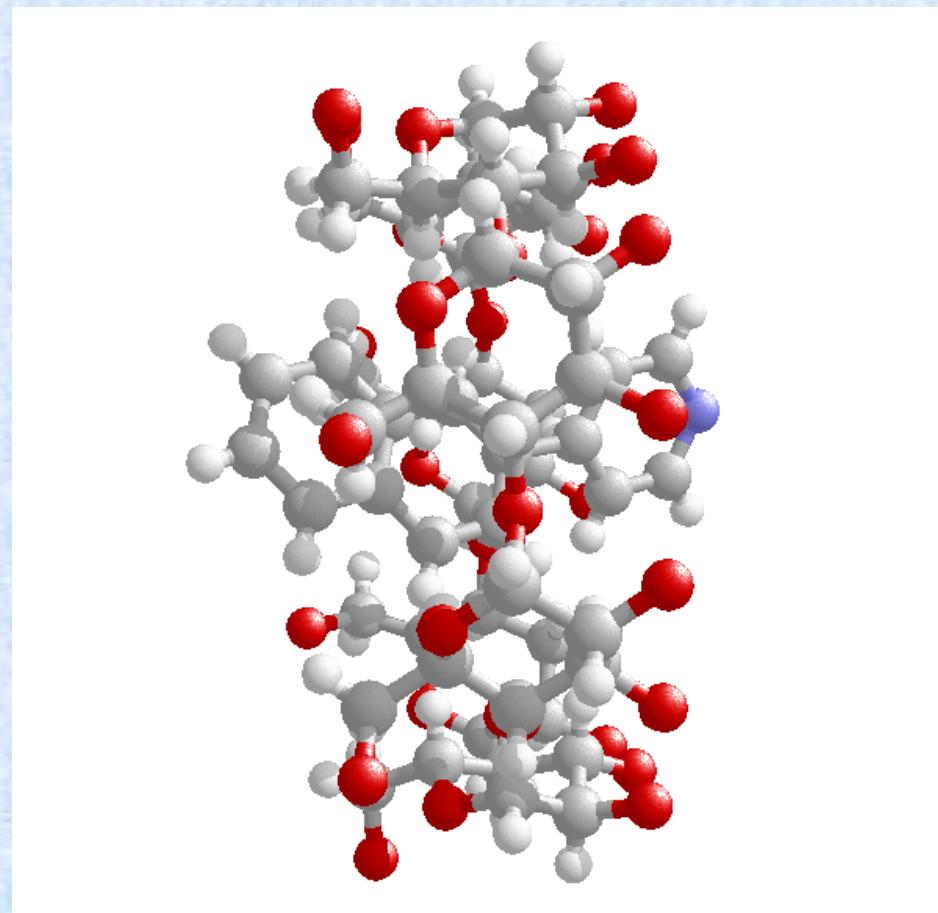
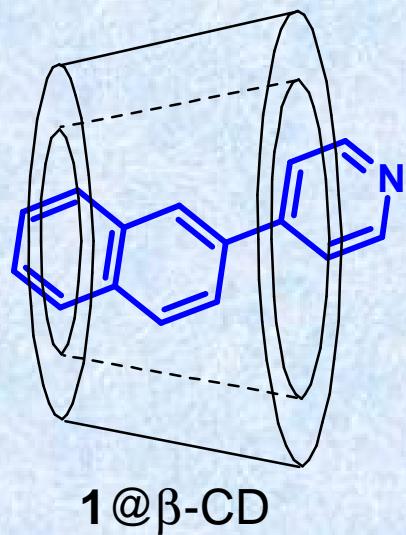
PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



Discovery of the reversible photoinduced mechanical displacement of naphthylpyridine in the β -cyclodextrin cavity allowed us to develop a new type of photocontrolled molecular machines.

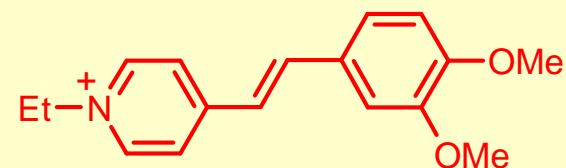
Russ. Chem. Bull. **2004**, 53, 2525;
J. Photochem. Photobiol. A **2011**, 217, 87;
Russ. Chem. Bull. **2013**, 62, 2150.

X-ray structure determination of photocontrolled supramolecular machine

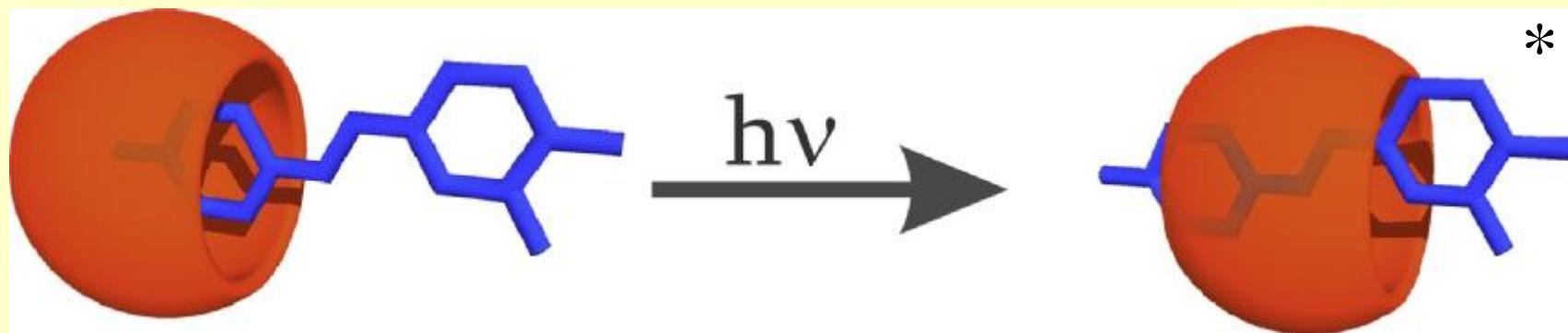


Russ. Chem. Bull. **2004**, *53*, 2525;
J. Photochem. Photobiol. **2011**, *217*, 87;
Russ. Chem. Bull. **2013**, *62*, 2150.

PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



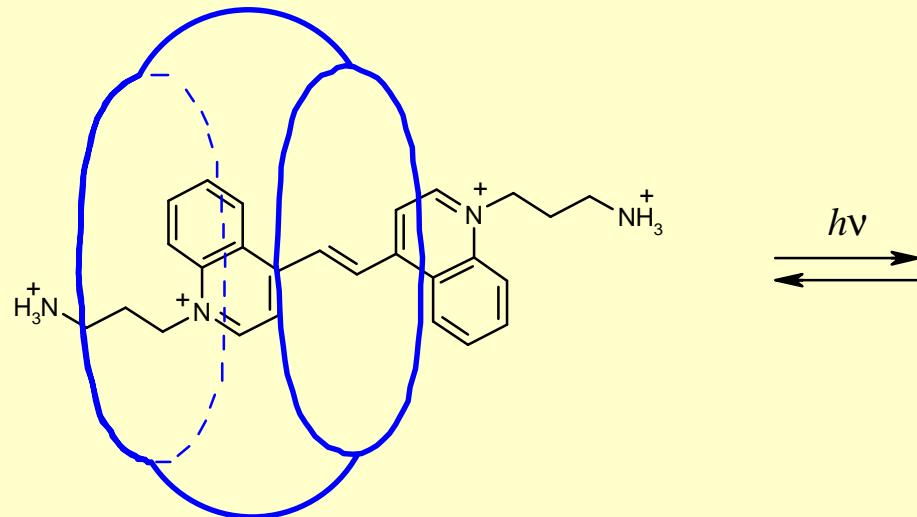
SD



SD@CB[7]

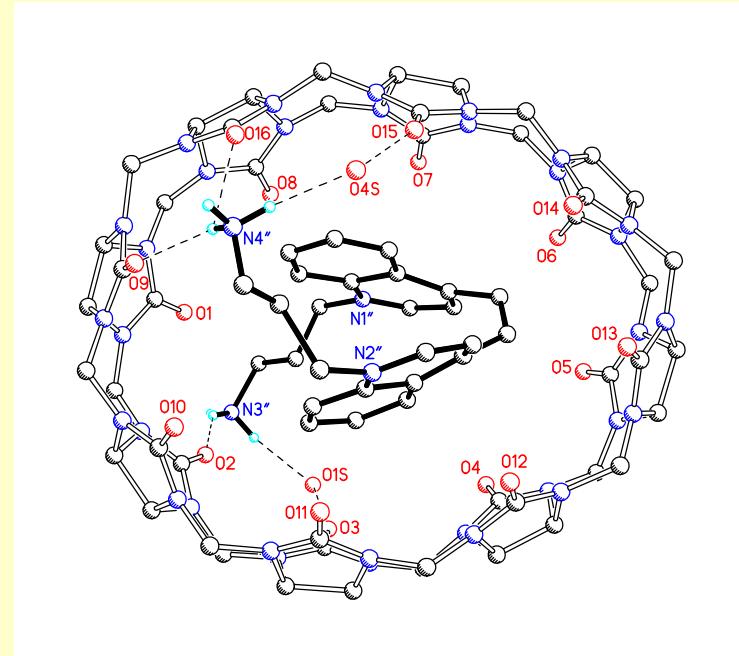
SD@CB[7] *

PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



trans-V@CB[8]

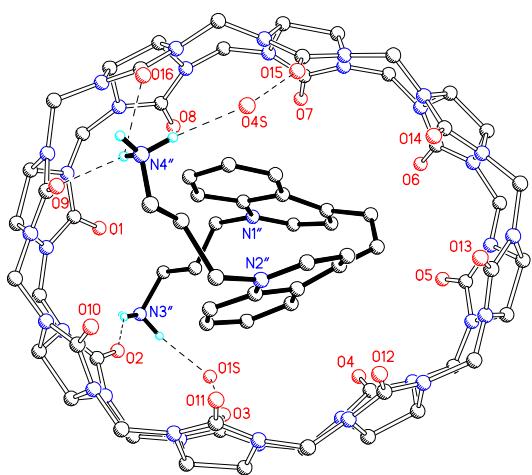
$$\log K = 4.6$$



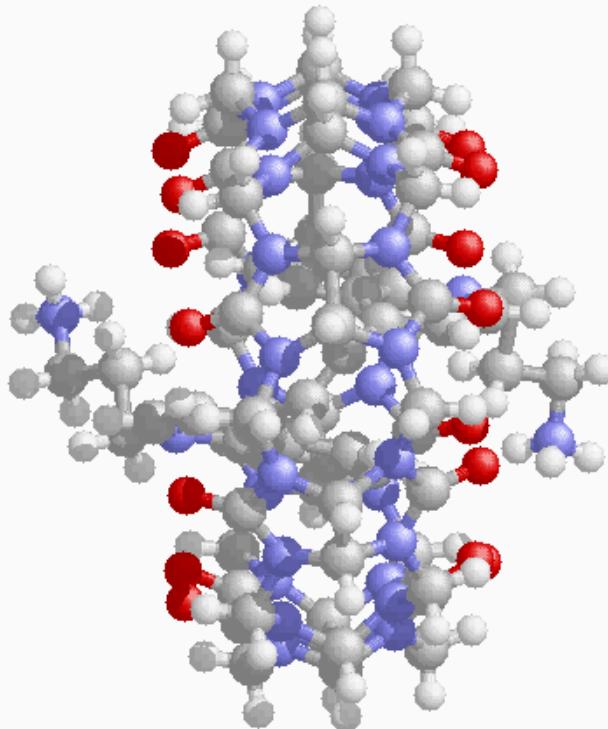
cis-V@CB[8]

Pseudorotaxane complexes of cucurbiturils and unsaturated viologen analogues as the design of new-type photocontrolled supramolecular machines

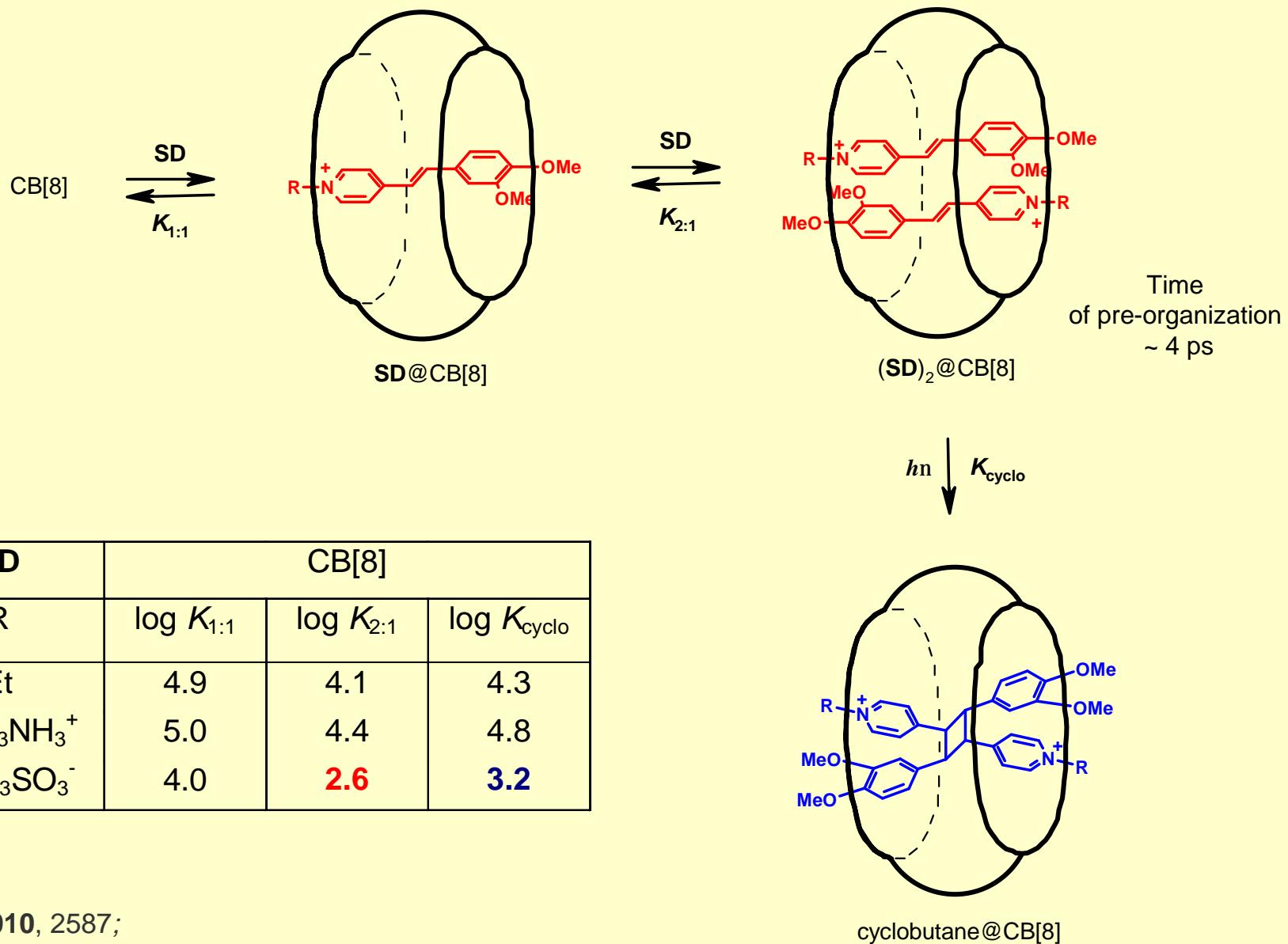
X-ray structure determination of photocontrolled supramolecular machine



cis-V@CB[8]

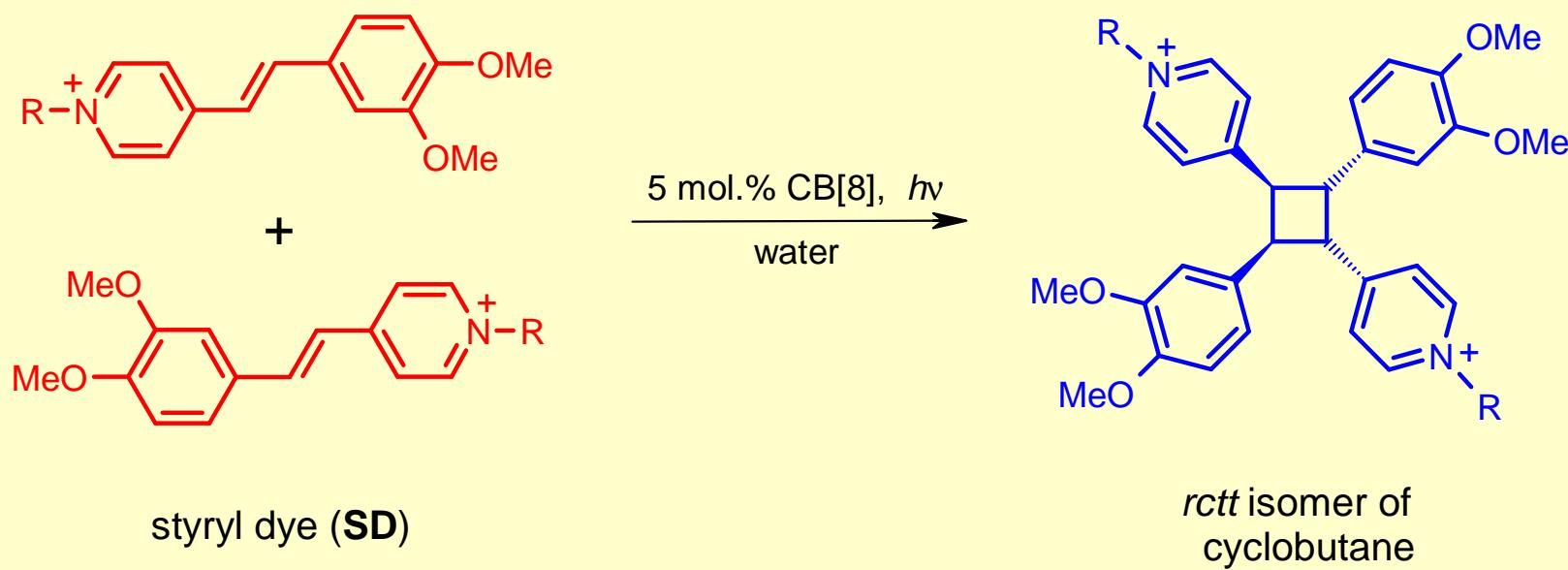


PHOTOCONTROLLED SUPRAMOLECULAR MACHINES

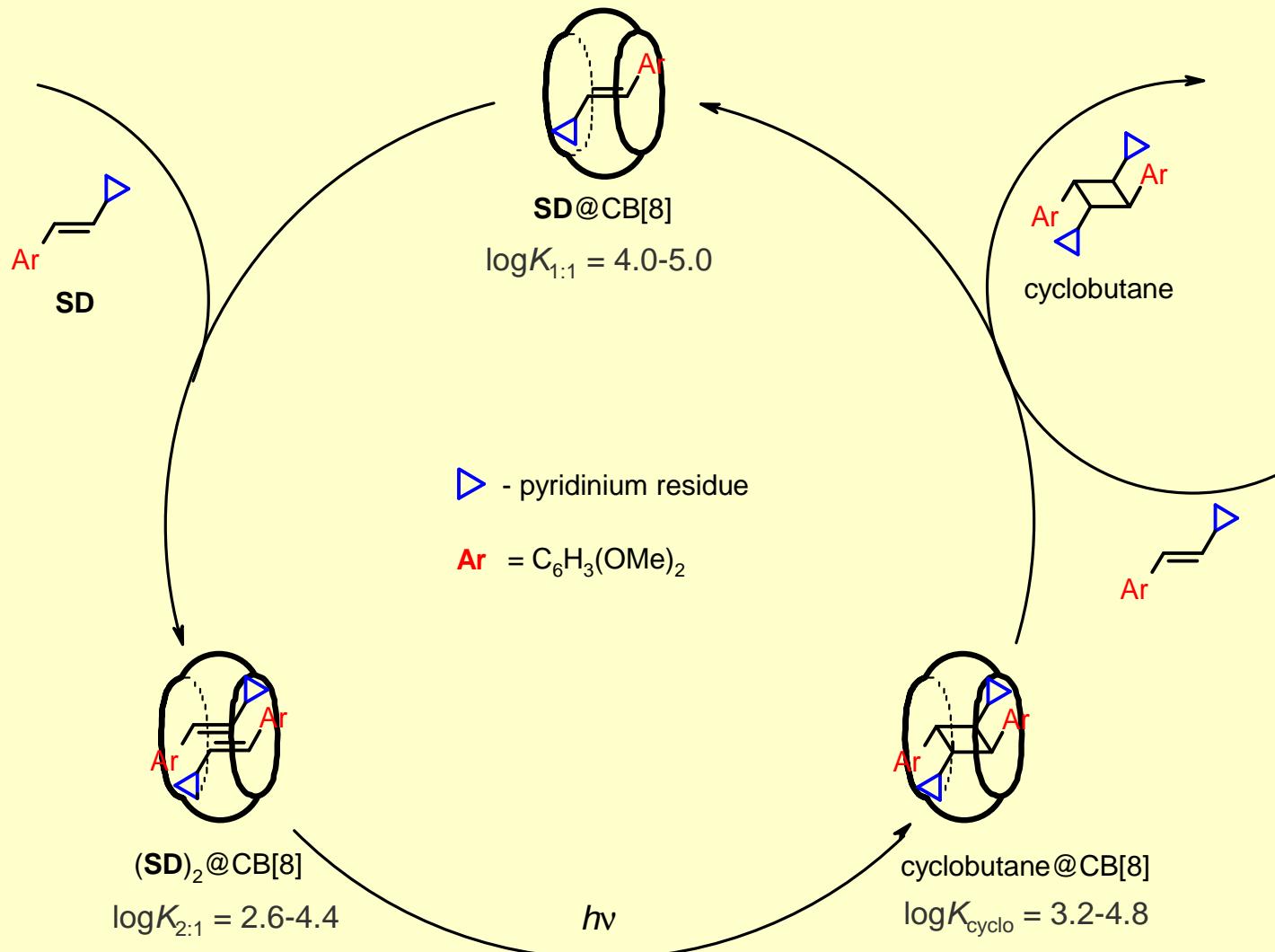


Eur. J. Org. Chem. 2010, 2587;
 J. Phys. Chem. A. 2011, 115, 4505;
 J. Photochem. Photobio. A. 2013, 253, 52;
 Chem. Phys. Lett. 2016, 647, 157.

PHOTOCONTROLLED SUPRAMOLECULAR ASSEMBLER BASED ON CUCURBIT[8]URIL

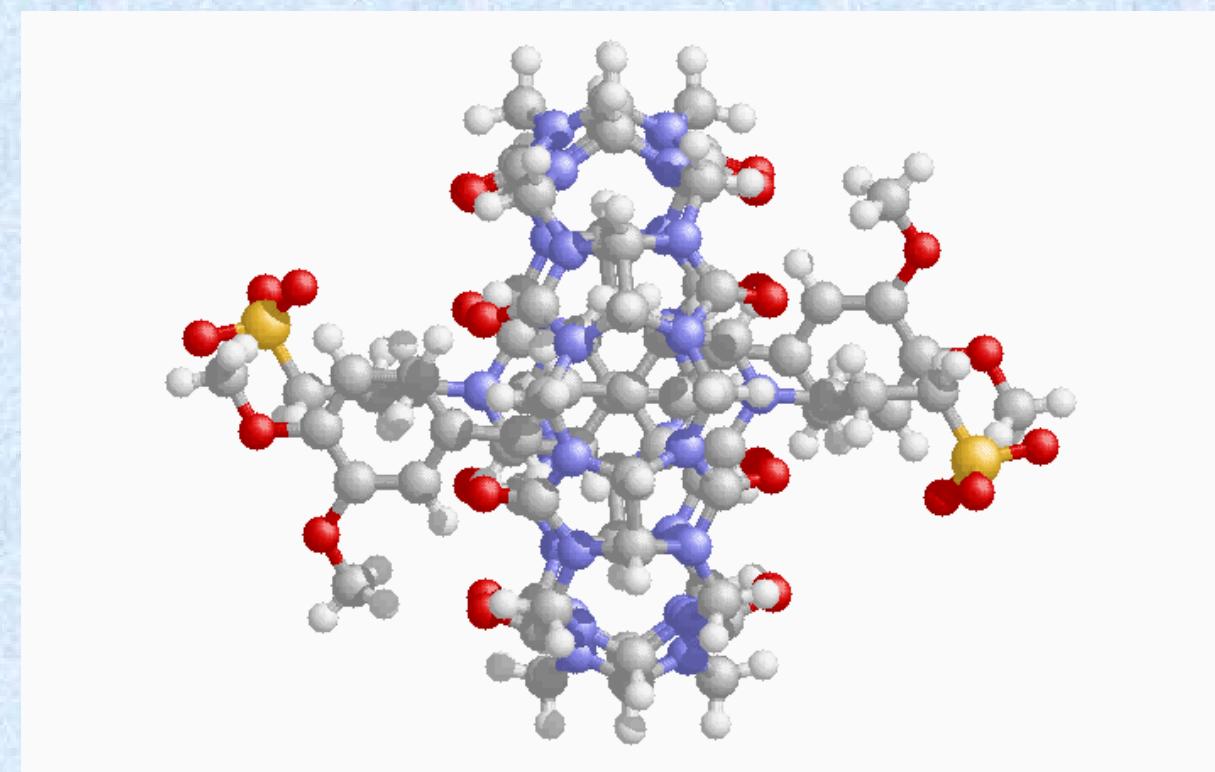
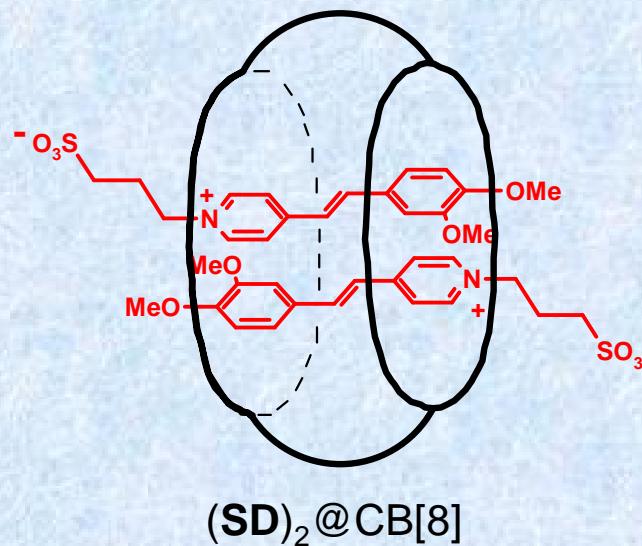


PHOTOCONTROLLED SUPRAMOLECULAR ASSEMBLER BASED ON CUCURBIT[8]URIL



Eur. J. Org. Chem., 2010, 2587;
J. Phys. Chem. A., 2011, 115, 4505;
High Energy Chem., 2014, 48, 253;
Chem. Phys. Lett. 2017, 673, 99.

X-ray structure determination of photocontrolled supramolecular assembler



It is possible to implement all main types of photoprocesses:

- § **Fluorescence, excimer formation**
- § **Photodissociation**
- § **Photoisomerization**
- § **Photocycloaddition**
- § **photoelectrocyclization**
- § **charge-transfer complex formation,
electron transfer**
- § **proton transfer**
- § **excitation transfer**
- § **TICT state**

Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

Ushakov E. N., Gromov S. P. et al. *Russ. Chem. Rev.* **2008**, 77, 39 (review);

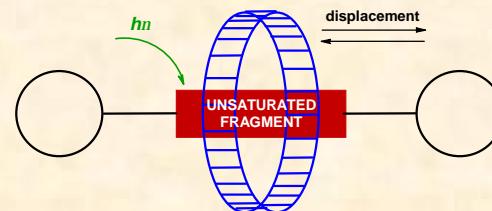
Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, 84, 787 (review).

Molecular meccano of photoactive supramolecular systems



Unique set of characteristics needed:

- § Accessibility through organic synthesis.
- § Tendency for spontaneous organization into various supramolecular architectures.
- § The ability to undergo different types of photochemical transformations depending on the structure.
- § The feature of high-efficiency molecular photoswitching.



Gromov S. P. Russ. Chem. Bull. 2008, 57, 1325 (review);
Gromov S. P. Rev. J. Chem. 2011, 1, 1 (review).

Applied potential: new strategy for the design of materials for nanophotonics

Demonstrated by an example of design:

- § **Photoswitchable supramolecular devices**
- § **Photocontrolled supramolecular machines**
- § **Supramolecular photoswitches**
- § **Optical chemosensor materials**
- § **Data optical recording and storage systems**
- § **Photochromic ionophores and photocontrolled membrane transport**
- § **Photoswitchable polymeric and LB films**
- § **Laser dyes**

Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

Ushakov E. N., Gromov S. P. et al. *Russ. Chem. Rev.* **2008**, 77, 39 (review);

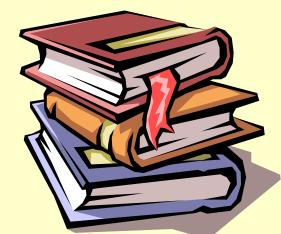
Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, 84, 787 (review).

Publications :

More than 320 publications in scientific journals and patents

Collaboration

- Institute of Problems of Chemical Physics of RAS
- Kurnakov Institute of General and Inorganic Chemistry of RAS
- Lomonosov Moscow State University, Chemical Department
- Institute of Bioorganic Chemistry of RAS
- Lomonosov Moscow State Academy of Fine Chemical Technology
- Zelinsky Institute of Organic Chemistry of RAS
- University of Durham, Great Britain
- Max-Planck-Institut fur Biophysikalische Chemie, Germany
- am Engler-Bunte Institut der Universitat Karlsruhe, Germany
- University of Umea, Sweden
- Bogatsky Physicochemical Institute of NAS, Ukraine
- North Carolina State University, U.S.A.
- The Florida State University, U.S.A.
- Universita' Degli Studi Di Bologna, Italy



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- Moscow Government (2003 - 2005)
- The Royal Society (1997 - 2017)
- INTAS (1993 - 2005)
- CRDF (1996 - 2004)
- DFG (1996 - 2004)
- ISF (1993 - 1994)



Российский
научный
фонд



Acknowledgment

Awards and Prizes:

State Prize of the Russian Federation (2018)

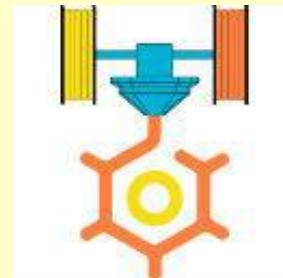


A. Butlerov prize of Russian Academy of Sciences (2006)



Scientific discovery of the USSR (1980)





Thank You

International Conference “Organic & Hybrid
Functional Materials and Additive
Technologies”